SPIROCYCLIC INTERMEDIATES IN THE REARRANGEMENTS OF ORGANOALKALI COMPOUNDS

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SUMMARY

The purpose of this research is to study the possible rearrangements of some organoalkali compounds (or carbanions) of lithium and cesium and to detect any reactive spiro intermediates. While spiro anions have long been suggested as intermediates or transition states in [1,2] migrations of aryl groups in organoalkali reactions, their presence has not been directly detected or observed.

Reaction of 3-p-biphenylyl-1-chloropropane, m.p. 32-33°, with Cs-K-Na alloy of eutectic composition in THF at -75° for 33 seconds gave a dark red solution which on carbonation yielded 36% of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (III), 14% of p-biphenylylacetic acid, 3% of 2-p-biphenylylbutanoic acid, and 4% of 4-p-biphenylylbutanoic acid. The yield of acid III decreased with time; the intermediate spiro anion had a half-life of about 13 minutes and disappeared on standing or raising the temperature of the reaction mixture. In contrast, reaction of the chloride with lithium in THF at -75° gave 3-p-biphenylylpropyllithium which was not appreciably rearranged even at -20°. Treatment of this organolithium reagent with CsO-t-Bu or KO-t-Bu in THF gave 3-p-biphenylylpropylcesium (or -potassium) which underwent 1,3-proton shift to form the more stable 1-p-biphenylylpropylcesium (or -potassium). Reaction of the chloride with Cs-K-Na in presence of 18-crown-6 also gave 1-p-biphenylylpropylcesium as the major product but also gave a good yield of the spiro acid III.

Though cyclopropyl and cyclobutyl rings have about the same total ring strain, reaction of 2-p-biphenylyl-1-chloropropane with Cs-K-Na alloy in THF at -75° for one minute gave less than 1% (if any) of the desired spiro anion even though some 60% of the starting chloride had been consumed.

Reaction of 2-p-biphenylyl-1-chloro-2-methylpropane, m.p. 63-64°, with Cs-K-Na alloy in THF at -75° for 70 seconds gave after carbonation a complex mixture of products of which the major volatile products were identified as 20% of 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII), 2.5% of 3-p-biphenylyl-3-methylbutanoic acid (IX), 3% of 4'-t-Bu-3-biphenylcarboxylic acid (X), and 10% of 4-p-biphenylyl-3-methyl-3-butenoic acid (XI). No products directly derived from a spiro anion were obtained. The olefinic acids VIII and XI are believed to be formed by α-elimination followed by proton abstraction from the olefin. Reaction of the chloride with lithium metal in THF at -75° gave mainly 2-p-biphenylyl-2-methylpropyllithium together with 10 to 15% of 2-p-biphenylyl-1,1-dimethylethyllithium. There was no isomerization of these organolithium compounds into one another under the reaction conditions tested. When this reaction was repeated in presence of t-BuOH, the same ratio of rearranged to non-rearranged products was found. These facts suggest that the rearranged organolithium compound was formed via rearrangement of an intermediate free radical.

Reaction of 1-p-biphenylyl-2-chloro-2-methylpropane, m.p. 97-97.5°, with Cs-K-Na alloy in THF at -75° gave besides some β-elimination products, a 79 to 21 ratio of rearranged to unrearranged products. Speculately, 2-p-biphenylyl-1,1-dimethylethylcesium was first formed,

then cyclized and re-opened to give the more stable 2-p-biphenylyl-2-methylpropylcesium. When the same reaction was run in THF in presence of MeOH, a 33 to 67 ratio of rearranged to unrearranged products were found. This result agrees with the idea that it is mostly the carbanion which is undergoing rearrangement and which is trapped prior to rearrangement by addition of MeOH. Reaction of the same chloride with lithium in THF at -75° gave relative yields of 67% of 2-p-biphenylyl-1,1-dimethylethyllithium and 33% of 2-p-biphenylyl-2-methylpropyllithium. When this lithium reaction was repeated in presence of t-BuOH, a 77 to 23 ratio of unrearranged to rearranged product was formed. Since there was no further rearrangement detected after the two organolithium compounds were formed, the possible pathway for the formation of the rearranged organolithium compound could be partly via a spiro radical and partly via a spiro anion only loosely bound to a lithium cation.

Reaction of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane, m.p. 110-111°, with lithium in THF at -75° gave after carbonation 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX). In contrast, reaction of this chloride with Cs-K-Na alloy in THF at -75° gave 7% of 3-p-biphenylyl-2.2.3-trimethylbutanoic acid (XX) and 28% of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXI) along with considerable nonvolatile acid. 1,1,2,2-Tetramethyl-6-phenylspiro-[2.5]octadienyl anion (XXXV) is regarded as a precursor of the acid XXI and has a half-life of about 22 minutes in THF at -75°. The open form 2-p-biphenylyl-1,1,2-trimethylpropylcesium (XXXIV) has the same half-life as XXXV. This and other evidence suggest that XXV and XXXIV are in mobile equilibrium. When the starting chloride was labeled

primarily with deuterium in the methyl groups nearest the chlorine, the open carboxylic acid XX from carbonation showed extensive deuterium label in the methyl groups nearest the biphenylyl group in about the amount expected for equilibration of the label in an intermediate carbanion. For a mobile equilibrium between XXXIV and XXXV, certain electrophilic reagents may attach one of the isomeric anions more readily than the other; this is believed to be the reason why reaction with trimethylsilyl chloride or dimethyl sulfate yielded only open chain trimethylsilylation or methylation product.

While the equilibrium between XXXIV and XXXV with cesium as cation the mixture consists of a 1:4 ratio respectively of the anions; with lithium as counter ion in THF only the open form 2-p-biphenylyl-1,1,2-trimethylpropyllithium was present according to the result of carbonation. Evidently lithium cation prefers to interact with the localized anion since such interaction can lead to the usual covalent organolithium compound.

CHAPTER I

INTRODUCTION

The purpose of this research is to study the possible rearrangements of some organoalkali compounds using lithium metal or Cs-K-Na alloy as the source of the alkali metal cation. The simplest reaction which a carbanion (i.e., an organoalkali compound) can undergo would appear to be a molecular rearrangement. The knowledge about the occurrence or non-occurrence of such a reaction would appear necessary for successful procedures using carbanions as synthetic reagents in organic synthesis for the formation of new carbon-carbon bonds.

Spiro anions have long been suggested as intermediates[1-3] or transition states in [1,2] migrations of aryl groups in arylalkyl anions. Spiro anions in [1,4] migrations[4-6] of aryl groups are now well documented. Suspected spiro anions in [1,2] or [1,3] migrations have not been observed or detected directly.

Grovenstein and Rhee[4] have reported that reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with Cs or K at 65° or with Cs-K-Na alloy at -75° gave 4-p-biphenylyl-1,1-diphenylbutyl anion as deduced from the NMR spectrum of the anion and the products of carbonation and

---

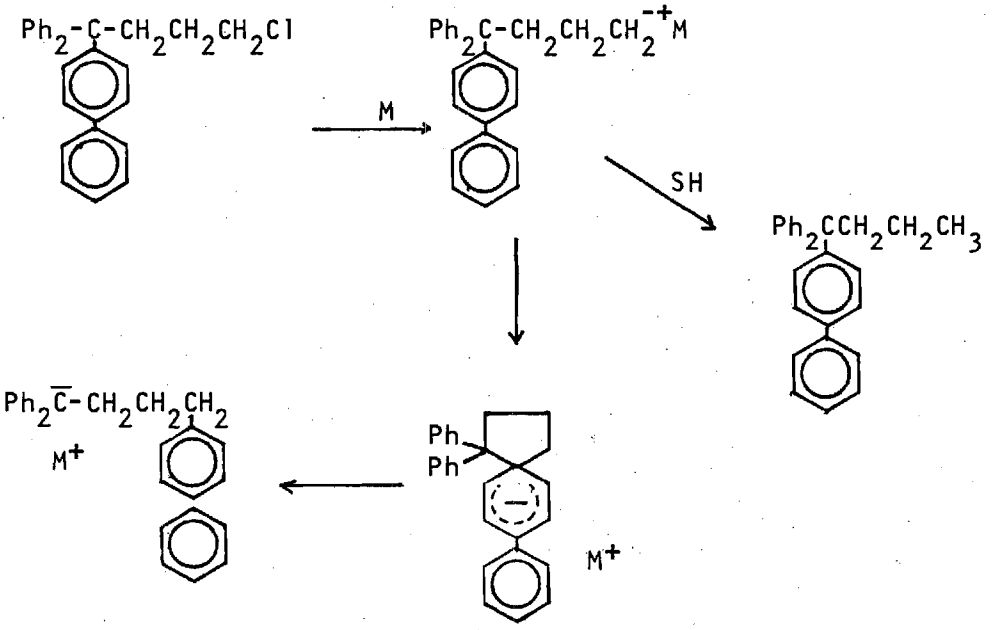
[1] H. E. Zimmerman and A. Zweig, J. Amer. Chem. Soc., 83, 1196 (1961).

[2] E. Grovenstein, Jr. and L. P. Williams, Jr., ibid., 83, 2537 (1961).

[3] E. Grovenstein, Jr. and G. Wentworth, ibid., 89, 2348 (1967).

[4] E. Grovenstein, Jr. and J. U. Rhee, ibid., 97, 769 (1975).

protonation. When the reaction was run in presence of a small amount of t-BuOH, the product was unrearranged 1-p-biphenylyl-1,1-diphenylbutane or products derived from the latter by subsequent reduction of the p-biphenylyl group. Likewise with sodium in refluxing dioxane the chloride gave 1-p-biphenylyl-1,1-diphenylbutane containing only some 7% of the rearranged



hydrocarbon 4-p-biphenylyl-1,1-diphenylbutane. In contrast to sodium, with K or Cs in dioxane chiefly the rearranged hydrocarbon was obtained. From these results they concluded that the chloride reacted with Na, K, Cs to give 4-p-biphenylyl-4,4-diphenylbutyl alkali metal compounds which is either readily protonated or undergo 1,4-migration of p-biphenylyl to give the more stable 4-p-biphenylyl-1,1-diphenylbutyl anion evidently via a spiro anion.

Grovenstein and Akabori[5] have reported that reaction of

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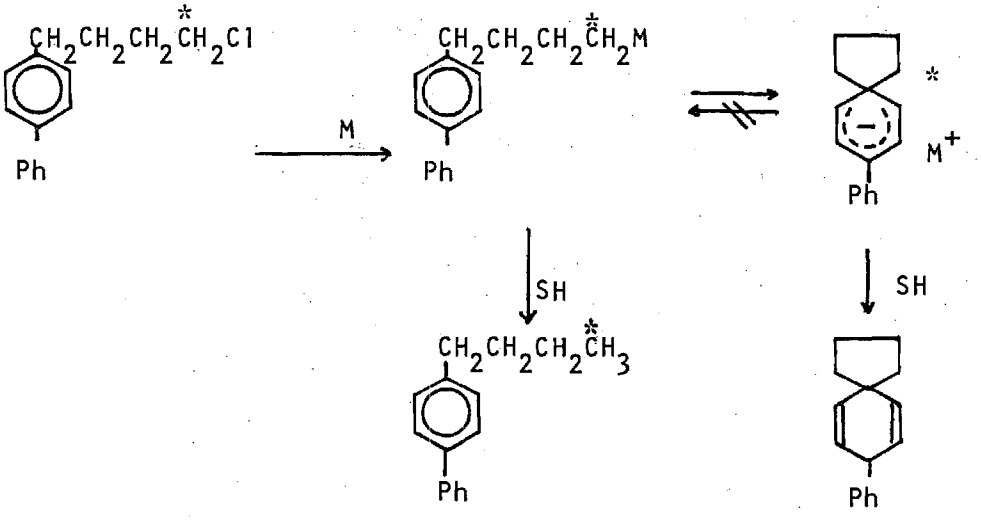
[5]E. Grovenstein, Jr. and S. Akabori, J. Amer. Chem. Soc., 97, 4620 (1975).

4-chloro-1-p-biphenylylbutane with lithium in THF at -70° gave a mixture of 4-p-biphenylylbutyllithium and 8-phenylspiro[4.5]-6,8-decadienyllithium; with K, Cs, and Cs-K-Na alloy chiefly the spiro anion and a little 1-p-biphenylylbutyl anion. Repetition of the reaction



with potassium in presence of t-BuOH resulted in non-rearranged p-biphenylylbutane, indicating that 4-p-biphenylylbutyl anion is a precursor of 8-phenylspiro[4.5]-6,8-decadienyl anion. From labeling experiments conducted with 4-p-biphenylyl-1-chlorobutane-1,1-d_2 no evidence was ever found for scrambling of the position of the label between the 1- and 4-positions.

Julia and Malassine[6] have reported that reaction of 4-chloro-n-butyl-p-benzoic acid with lithium in liquid ammonia gave 60% of spiro[4.5]deca-6,9-diene-8-carboxylic acid and 38% of n-butyl-p-(1,4-dihydro)benzoic acid; in the presence of ethyl alcohol the same products were obtained in the same yield.

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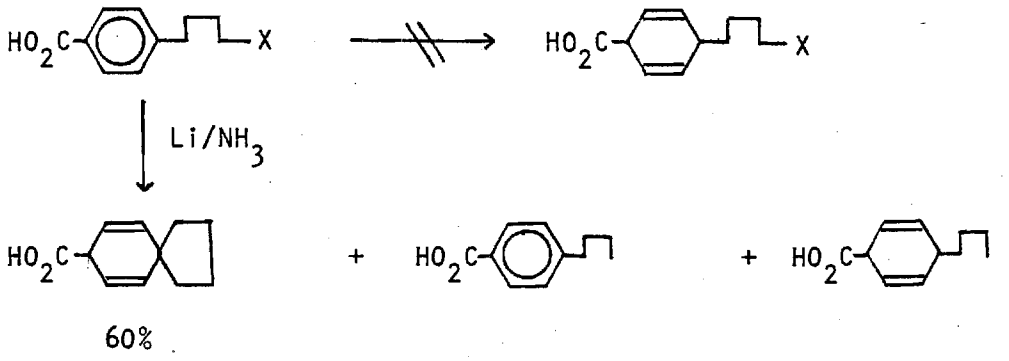
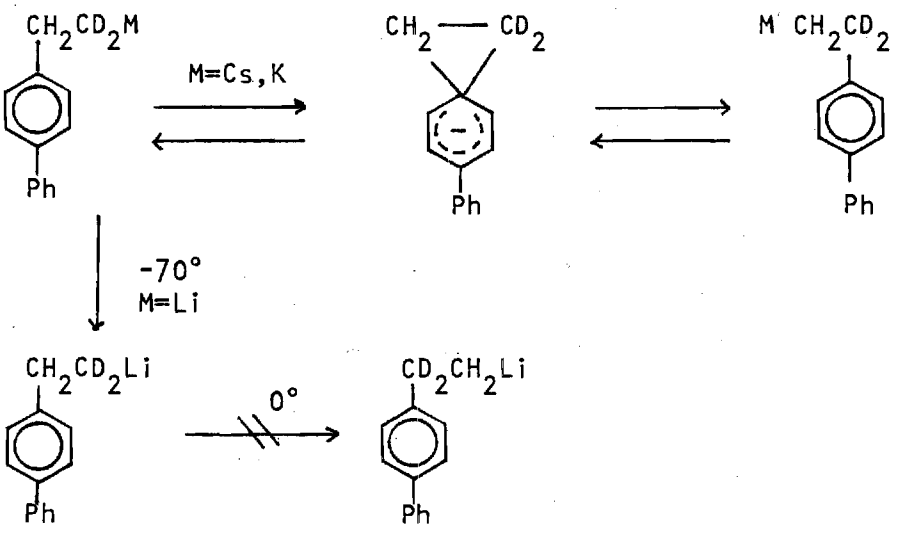
[6] M. Julia and B. Malassine, Tetra. Lett., 24, 2495 (1972).



Grovenstein and Cheng[7] have reported that reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with excess lithium metal in THF solution at -70° gave a good yield of 2-p-biphenylylethyllithium-1,1-d_2, which did not undergo appreciable rearrangement on warming to 0° as judged by the position of the deuterium label in the products of carbonation and protonation. In contrast, reaction of the same chloride with cesium or potassium metal in THF at reflux temperature gave essentially a 50/50 mixture of 1-p-biphenylylethane-2,2-d_2 and 1-p-biphenylylethane-1,1-d_2; in reaction of the chloride at -65° with Cs-K-Na alloy, scrambling



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[7] E. Grovenstein, Jr. and Y.-M. Cheng, J. Amer. Chem. Soc., 94, 4971 (1972).

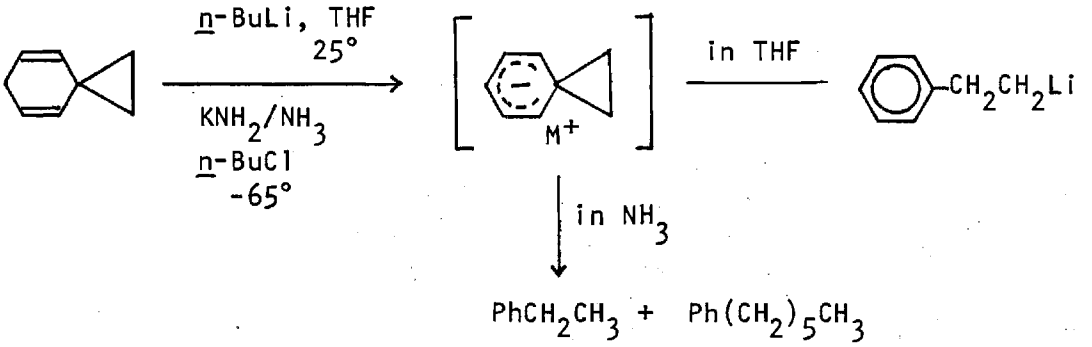
of the label in the p-biphenylylethane was only partial; repetition of the reaction with potassium in presence of a small amount of t-BuOH resulted in a greatly reduced amount of rearrangement in the product p-biphenylylethane. Since formation of 2-p-biphenylylethyl anion preceded appreciably rearrangement, they found no evidence for participation of p-biphenylylradical anion (or dianion) as a powerful nucleophile which displaced chloride to give directly the spiro radical (or corresponding anion). They also have reported[8] that reaction of 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) with lithium metal in THF at -65° gave, according to the results of carbonation, 2-methyl-2-phenylpropyllithium containing 6.4% of 1,1-dimethyl-2-phenylethyllithium (product of 1,2-phenyl migration). Since warming their reaction mixture to 4° gave chiefly the corresponding hydrocarbons without increase in the amount of phenyl migration product, the organolithium compound from neophyl chloride did not rearrange to 1,1-dimethyl-2-phenylethyllithium. They suggested that the observed rearrangement took place in an intermediate, presumably the neophyl radical, prior to formation of the organolithium reagent.

Staley and coworkers[9] have reported an attempt to generate spiro[2.5]octa-4,6-dienyl anion by reaction of spiro[2.5]octa-4,6-diene with potassium amide in liquid ammonia at -65° or with n-BuLi in THF-hexane at room temperature; however, they obtained only products in which the cyclopropane ring was opened. It is not clear from these

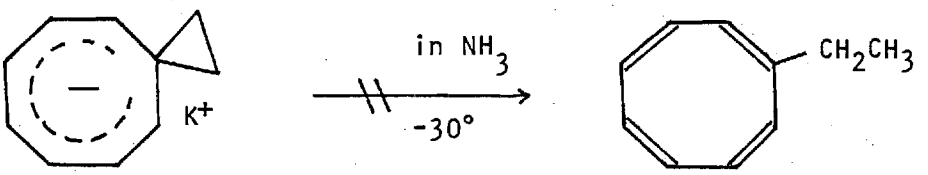
---

[8] E. Grovenstein, Jr. and Y. -M. Cheng, Chem. Comm., 101 (1970).

[9] S. W. Staley, M. Cramer and W. G. Kingsley, J. Amer. Chem. Soc., 95, 5052 (1973).



experiments whether the spiro anion was an intermediate or a transition state; however, the related species spiro[2.7]decatrienyl anion could be prepared in liquid ammonia and was stable in this solvent at -30°.



The comparative stability of this spiro anion toward ring opening is attributable to the fact that the product would be a non-aromatic cyclooctatetraene derivative whereas the product from the previous spiro anion is aromatic.

Eisch and Kovacs[10] have reported a spiro compound from reaction of the N-methiodide of 2-methyl-2-(4-pyridyl)propyl chloride with Li in THF. Fraenkel and Cooper[11] have also reported that reaction of 2-(4-pyridyl)-2-methylpropyl metal derivatives (Mg, Li, and Hg) with

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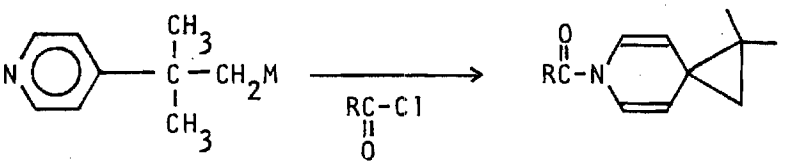
[10]J. J. Eisch and C. A. Kovacs, J. Organomet. Chem., 25, C33 (1970).

[11]G. Fraenkel and J. W. Cooper, J. Amer. Chem. Soc., 93, 7228 (1971).



acyl chlorides gave stable ring closure products, 1-1-dimethyl-6-acyl-6-azaspiro[2.5]octa-4,7-diene.

In the present work, the reactions of 3-p-biphenylyl-1-chloropropane and 2-p-biphenylyl-1-chloroethane with alkali metals were studied, in hope of observing the formation of spiro anions. The products from these reactions were reacted with solid carbon dioxide to convert the organoalkali compounds to carboxylic acids. These acids were then converted to the corresponding methyl esters by reacting with diazomethane and the esters analyzed by quantitative gas chromatography (G.C.). The hydrocarbons accompanying the acids were also analyzed by G. C.

While reaction[7] of the lower homolog 1-p-biphenylyl-2-chloroethane-1,1-d_2 with Cs-K-Na alloy in THF at -75° gave products showing scrambling of the label (or rearrangement of the p-biphenylyl group), the suspected spiro anion was not detected in the present work. A method was sought to increase the stability of the possible spiro anion. A possible method is to make use of the Thorpe-Ingold or "gem-dimethyl" effect which, in one statement,[12] is that "the accumulation of substituents along the chain of a bifunctional system appears to selectively

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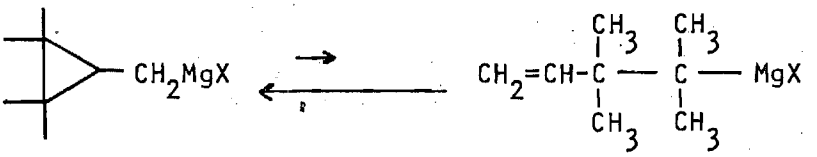
[12] G. S. Hammond, in Steric Effects in Organic Chemistry, M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 460-469.

stabilize the corresponding cyclic forms." Maercker and coworkers[13] have recently used this effect to shift the equilibrium between a 3-butenyl Grignard reagent and a cyclopropylmethyl Grignard reagent in favor of the cyclopropylmethyl compound.



In the present work, the reactions of the dimethyl derivatives of 2-p-biphenylyl-1-chloroethane, namely 2-p-biphenylyl-1-chloro-2-methylpropane and 1-p-biphenylyl-2-chloro-2-methylpropane, with alkali metals were examined. Since the Thorpe-Ingold effect is expected to be larger for four methyl groups than for two, the reactions of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane with alkali metals were also studied.

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[13] A. Maercker, P. Güthlein and H. Wittmayr, Ang. Chem. Int. Ed. Engl., 12, 774 (1973).

CHAPTER II

REAGENTS AND SOLVENTS

4-Acetylbiphenyl

Aldrich grade 4-acetylbiphenyl (m.p. 112-114°) was recrystallized from ethanol to give a sample, m.p. 119-120°.

Aluminum Chloride

Fisher certified anhydrous aluminum chloride was used without further purification.

Ammonium Chloride

Baker reagent grade ammonium chloride was used.

Benzene

Fisher certified (thiophene free) benzene was used.

Biphenyl

Aldrich or Eastman biphenyl was used without further purification.

4-Biphenylacetonitrile

Aldrich 4-biphenylacetonitrile (m.p. 89-92°) was used.

4-Biphenylcarboxylic Acid

Aldrich 4-biphenylcarboxylic acid (m.p. 222-224°) was recrystallized from Ligroin (b.p. 90-102°) to give crystals, m.p. 227-228°.

p-Bromobiphenyl

Eastman white label grade p-bromobiphenyl was used without further purification.

t-Butyl Alcohol

Fisher certified t-butyl alcohol was used without further purification.

t-Butyl Chloride

Eastman white label t-butyl chloride (2-chloro-2-methylpropane) was used.

n-Butyllithium

Ventron n-butyllithium in n-hexane (22%, 2.6 M) was used without further purification.

iso-Butyric Anhydride

Eastman technical iso-butyric anhydride was redistilled at 181.0-182.5°.

Carbon Disulfide

Baker reagent grade carbon disulfide was used.

Carbon Tetrachloride

Fisher certified carbon tetrachloride was used.

Cesium

MSA research Corp., 99.9 percent minimum purity cesium was used.

1-Chlorobutane

Columbia grade 1-chlorobutane was redistilled at 76-77° through a 60 cm vacuum jacketed column packed with glass helices.

Chloroform

Fisher certified chloroform was used.

Chloroform-D

Merck Sharp and Dohme of Canada Ltd. chloroform-d was used.

Chlorotrimethylsilane

Aldrich chlorotrimethylsilane was redistilled at 58°.

18-Crown-6

Peninsular Chem. Research, Inc. 18-crown-6 (m.p. 38-39°) was used.

Cyclohexane

Fisher certified cyclohexane was used.

Diazald

Aldrich 99% diazald (m.p. 59-61°) was used.

Diethyl Ether

Fisher anhydrous grade diethyl ether was stored over sodium wire.

Diethyl Phthalate

Matheson diethyl phthalate was found to be pure by G. C. analysis.

Dimethylsulfoxide-d_6

Merck Sharp and Dohme dimethylsulfoxide-d_6 (minimum atom % D, 99.5%) was used.

Dimethyl Sulfate

Aldrich gold label 99+% dimethyl sulfate was used.

Dipentyl Phthalate

Eastman practical dipentyl phthalate was found to be pure by G. C. analysis.

Dipropyl Phthalate

Eastman white label dipropyl phthalate was found to be pure by G. C. analysis.

Ethyl Alcohol

Commercial grade ethyl alcohol was used.

Hexane

Fisher certified hexane was used.

Iodomethane

Aldrich 99 percent iodomethane (b.p. 41-43°) was used.

Iodomethane-d_3

Aldrich gold label (99+ atom % D) iodomethane-d_3 was used.

Lithium

Lithium Corporation of America, 0.05 percent sodium max., and Foote Mineral Co., 1 percent sodium, lithium wires were used.

Lithium Aluminum Hydride

Ventron lithium aluminum hydride was used.

Lithium Bromide

Coleman and Bell lithium bromide was used.

Magnesium

Fisher magnesium was used.

Magnesium Sulfate

Fisher certified anhydrous magnesium sulfate was used.

Mercuric Acetate

Fisher certified mercuric acetate was used.

Methallyl Chloride

Baker purified grade methallyl chloride was redistilled at 70.5-72° through a 60 cm vacuum jacketed-column packed with glass helices.

Methanol

Commercial grade methanol was purified by treatment with magnesium at reflux and then distilled at 64° through a 30-cm Vigreux column.

3-Methylbiphenyl

Aldrich 95 percent 3-methylbiphenyl was used.

2-Methyltetrahydrofuran

Aldrich 2-methyltetrahydrofuran was stored over sodium wire.

Morpholine

Aldrich morpholine was redistilled at 127-129°.

n-Pentane

Phillips Petroleum Co., pure grade n-pentane (99 percent minimum) was used.

Potassium

Fisher potassium metal stick was used.

Potassium Permanganate

Baker reagent grade potassium permanganate was used.

Potassium Hydroxide

Fisher certified potassium hydroxide was used.

Propionyl Chloride

Aldrich 97 percent propionyl chloride was used.

Pyridine

Fisher certified pyridine was stored over potassium hydroxide pellets.

Sodium

Baker purified sodium was used.

Sodium Aluminum Hydride

Ventron sodium aluminum hydride was used.

Sodium Borohydride

City Chemical Corp., 98% minimum, sodium borohydride was used.

Sodium Hydride

Ventron sodium hydride in 50% oil dispersion was used.

Sodium-Potassium

MSA Research Corp. sodium-potassium alloy containing 78% of potassium and 22% of Na was used.

Sulfur

Fisher USP precipitated sulfur was used.

Sulfuric Acid

Fisher reagent grade sulfuric acid was used.

Tetrahydrofuran

Fisher certified or Baker reagent grade tetrahydrofuran was stored over sodium wire.

Thionyl Chloride

Fisher reagent grade thionyl chloride was purified according to the published procedure.[14]

Triethanolamine

Fisher certified triethanolamine was used.

Trimethyloxonium Tetrafluoroborate

Cationics, Inc., trimethyloxonium tetrafluoroborate was used.

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[14]Weygand and Hilgetag, Preparatory Organic Chemistry, John Wiley & Sons, Inc., New York, N. Y., 1972, p. 226.

CHAPTER III

GENERAL PROCEDURE FOR REACTIONS AND INSTRUMENTAL ANALYSES OF PRODUCTS

General Procedure

Reactions with alkali metals were normally conducted in a 500-ml Morton flask equipped with a Morton high-speed stirrer,[15] a condensor and an addition funnel. The apparatus was flame-dried under a stream of dry nitrogen. For reactions of Cs-K-Na alloy and Na-K alloy the entire apparatus were contained in a glove box under an atmosphere of nitrogen. In some reactions of organolithium compound with potassium t-butoxide, two sets of the usual apparatus were arranged side by side so that the reaction mixture could be siphoned from one flask into the other without being exposed to the atmosphere. Ethereal solvents were freshly distilled into the reaction flask from $LiAlH_4$ or $NaAlH_4$ under a nitrogen atmosphere before use. The reaction solvent was usually stirred with the metal at reflux temperature or room temperature (if the metal is liquid) for about one hour before addition of alkyl halide; this procedure provided finely divided alkali metal and also ensured that the solvent was free of impurities. After reaction, the solution was normally forced onto solid carbon dioxide; solid carbon dioxide was also added to the residual contents of the reaction flask. Finally

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[15] A. A. Morton and L. S. Redmon, Ind. Eng. Chem., 40, 1190 (1948).

excess EtOH was added to destroy unreacted alkali metal.

The Usual Work-Up Procedure for Products of Organometallic Reactions

The solvent was removed on a rotary evaporator, water was added, and the mixture was then extracted with ether. The ethereal layer was extracted with 5% KOH solution, was washed with water, and finally was dried over magnesium sulfate. After filtration the ethereal solution was concentrated on a rotary evaporator to yield neutral product. The alkaline extract was acidified with hydrochloric acid and then extracted with ether. The ethereal layer was washed with water and dried over magnesium sulfate. After filtration solvent was removed on a rotary evaporator to give acidic product.

Instrumental Analysis

The UV spectra were determined with a Cary Model 14 or a Perkin-Elmer 202 recording spectrophotometer. The ^{1}H NMR spectra were determined at 60 MHz on either a Varian A-60 or a T-60A NMR spectrometer and the ^{13}C NMR spectra were recorded at 25 MHz with a JEOL Fourier transform spectrometer, Model PFT-100; both spectra were made with tetramethylsilane as an internal standard. The mass spectra were run upon either a Varian M-66 or a Hitachi (Perkin-Elmer) RMU-7L mass spectrometer.

Gas chromatographic analysis of the reaction products were accomplished by using a Perkin-Elmer Model 881 Gas Chromatograph (P-E) with columns either 6 ft length, 1/8 inch outside diameter packed with 3 %

silicone Gum Rubber (SE-30) or 6 ft length, 1/4 inch outside diameter, packed with 5 % Silicone Gum Rubber, on 100-200 Mesh Chromosorb G-AW-DMCS (Chromosorb G, acid-washed and treated with dimethyldichlorosilane).

Quantitative gas chromatographic analyses of the reaction products were accomplished by adding a known amount of an internal standard compound to two solutions, one containing a known amount of product and the other containing a known amount of authentic sample. These two solutions were injected separately into the G. C. machine under the same conditions. Calculations were based on the assumption that the G. C. response factor of a compound in the authentic sample solution, calculated from the area to weight ratio of this compound to area to weight ratio of the internal standard, is identical to the response factor of that same compound in the product solution. The yields of products were expressed in mole % yield ("absolute yield") based upon the moles of starting organic reactant alkyl chloride unless otherwise specified. If only the relative compositions of the volatile products were determined, only G. C. area precent yields were calculated ("relative yield").

When a reaction solution was carbonated by fractions at different time intervals, the yields for each carbonated fraction are based on the amount of starting chloride estimated to have been present as judged by the weights of acidic and neutral products. The G. C. retention times of all the products from reactions of the alkyl chlorides with alkali metals, and the G. C. operating conditions are listed in

Appendix B. The term "known sample" refers to either a commercial sample, or a new compound which is fully characterized by spectroscopic data and elemental analysis and is given in this thesis.

CHAPTER IV

EXPERIMENTAL DETAILS

Synthesis of 3-p-Biphenylyl-1-chloropropane

1-p-Biphenylyl-1-oxo-propane

The title compound was prepared following the general procedure of Long and Henze.[16] In a typical run, starting with 61.7 gm (0.399 mole) of Biphenyl, 41.0 gm (0.442 mole) of propionyl chloride, and 58.9 gm (0.441 mole) of aluminum chloride there was obtained 73.3 gm (0.349 mole, 87.4%) of crude 1-p-biphenylyl-1-oxo-propane, m.p. 88-90°. Recrystallization from acetone gave 52.4 gm (0.250 mole, 62.3%), m.p. 90-91°. In another run, 124 g (0.803 mole) of biphenyl was allowed to react with 119 g (0.893 mole) of aluminum chloride and 81.5 g (0.881 mole) of propionyl chloride to give 143 g (0.681 mole, 84.9%) of crude product.

3-p-Biphenylylpropanoic Acid

The title compound was prepared following the general procedure of Schwenk and Papa.[17] To a 500 ml round bottom flask was put 125 ml of freshly distilled morpholine, 20.8 g (0.649 mole) of sulfur and 81.6 g (0.388 mole) of 1-p-biphenylyl-1-oxo-propane. The solution was heated at reflux for sixteen hours. While still hot, the solution was

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[16] L. M. Long and H. R. Henze, J. Amer. Chem. Soc., 63, 1939 (1941).

[17] E. Schwenk and D. Papa, J. Org. Chem., 11, 798 (1946).

poured into 500 ml of methanol. A yellow precipitate formed on cooling and upon filtration amounted to 86.0 g (0.327 mole, 84.3%) of thiomorpholide. To a 500 ml round bottom copper flask was put 26.3 g (0.100 mole) of the thiomorpholide, 188 ml of 70% ethyl alcohol and 38 ml of 50% sodium hydroxide solution. This solution was heated at reflux for seventeen hours. Alcohol was then removed on a rotary evaporator and water added to the residue. After neutralization with hydrochloric acid and treating with charcoal, the hot solution was filtered. The filtrate, on acidification, gave 19.2 g (84.9% from thiomorpholide) of product, m.p. 139-142°, which after recrystallization from acetic acid amounted to 13.9 g of crystals, m.p. 142.5-144.0°, literature m.p. 145°.[18]

3-*p*-Biphenylyl-1-propanol

The title compound was prepared by lithium aluminum hydride reduction of 3-*p*-biphenylylpropanoic acid in a 500-ml Morton flask fitted with a high-speed stirrer. A solution of 29.0 g (0.128 mole) of the acid in 90 ml of tetrahydrofuran was added to a suspension of 28.2 g (0.742 mole) of lithium aluminum hydride in 300 ml of freshly distilled tetrahydrofuran dropwise over a period of 45 minutes. The mixture was stirred at reflux for another three hours, then 40 ml of water mixed with 20 ml of THF was added dropwise to decompose unreacted lithium aluminum hydride. The reaction mixture was then poured into 400 ml of a 1:1 mixture of 6*N* hydrochloric acid and ice, and extracted with four 150-ml portions of ether. The ethereal extracts were

[18]Willgerodt and Schotz, *J. Prakt. Chem.*, (2), *81*, 397 (1910).

combined, washed with three 100-ml portions of 5% sodium bicarbonate solution and two 100-ml portions of water, dried over anhydrous magnesium sulfate, and filtered. After removing the solvent there was obtained 21.0 g (0.0989 mole, 77.3%) of crude product with m.p. 60-65°. One recrystallization from carbon tetrachloride gave 12.9 g of white crystals, m.p. 65-66°. The product was sublimed and then recrystallized from carbon tetrachloride to give crystals: m.p. 72.0-72.5°; ^{1}H NMR ($CDCl_3$), δ 7.40 (9 H, m), 3.63 (2 H, t, J = 6.5 Hz), 2.75 (1 H, s), 2.72 (2 H, t, J = 7 Hz), 1.88 (2 H, quint, J = 7Hz); λ_{max} (EtOH) 252 nm (ε = 19900); mass spectrum, m/e(rel. int.): 212 (58, M^+), 195 (6, $C_{15}H_{15}^+$), 194 (33), 181 (7), 167 (100); ^{13}C NMR ($CDCl_3$), δ 140.9, 138.7, 128.8, 128.7, 127.1, 127.0, 61.9, 34.1, 31.7.

Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.87, 84.78; H, 7.82, 7.83.

In another run, 74.4 g (0.330 mole) of the acid was reduced with 45 g (1.20 mole) of lithium aluminum hydride in a similar manner giving 97% of crude yield of the desired carbinol.

3-p-Biphenylyl-1-chloropropane

The title compound was synthesized through a modified procedure of McMahan and Bunce.[19] Into a 500 ml round-bottom flask, equipped with a mechanical stirrer, a dropping funnel, and a condensor of which the top was connected to an oil bubbler, were put 30.2 g (0.144 mole) of 3-p-biphenylyl-1-propanol and 11.4 g (0.145 mole) of pyridine. To

*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[19]M. A. McMahon and S. C. Bunce, J. Org. Chem., 29, 1515 (1964).

this solution was added 60.3 g (0.564 mole) of thionyl chloride dropwise during a period of 140 minutes at 0°. The solution was then heated on a steam bath for 20 minutes and finally poured into 600 ml of crushed ice. Ether extraction yielded 29.7 g (0.129 mole, 89.6%) of crude product, m.p. 31-32°, which was sublimed to give 28.7 g of white crystals of m.p. 32-33°; ^{1}H NMR ($CDCl_3$) δ 7.40 (9 H, m), 3.49 (2 H, t, J = 6.5Hz), 2.81 (2 H, t, J = 7 Hz), 2.11 (2 H, quint, J = 7 Hz); λ_{max}(EtOH) 253 nm (ε 25500); mass spectrum m/e (rel. int.), 232 (12, $M^+ + 2$), 230 (39, M^+), 195 (1, $C_{15}H_{15}^+$), 167 (100), 153 (7).

Anal.* Calcd. for $C_{15}H_{15}Cl$: C, 78.09; H, 6.55; Cl, 15.36. Found: C, 78.12, 78.13; H, H.59, 6.60; Cl, 15.25, 15.24.

Synthesis of 2-p-Biphenylyl-1-chloro-2-methylpropane

The title compound was synthesized following a general procedure of Whitmore, et al.[20] To a 1000-ml Morton flask equipped with a high-speed stirrer, a condensor, and an addition funnel were added 188 g (1.22 mole) of biphenyl in 250 ml of carbon disulfide and 10 ml of saturated sulfuric acid (95-98%). The solution was kept under a nitrogen atmosphere. To this solution was added dropwise over a period of eight hours 44.6 g (0.493 mole) of methallyl chloride diluted with 20 ml of carbon disulfide via a constant drop-rate addition funnel (Kontes Glass Co.) and then the solution was stirred for another ten hours. The organic layer was separated, washed twice with

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[20]F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, Jr., J. Amer. Chem. Soc., 65, 1469 (1943).

150-ml portions of 5% sodium bicarbonate solution to give 229 g of crude product which contained five peaks on G. C.. The product was fractionally distilled and the first fraction (176 g) was identified as biphenyl. The second fraction collected at 0.025 mmHg and 155-185° (bath temp) was identified as the expected product (43 g, 35% yield based on methallyl chloride) which was recrystallized twice from cyclohexane to give crystals of m.p. 63-64°; ^{1}H NMR ($CDCl_3$): δ 7.50 (9 H, m), 3.67 (2 H, s), 1.46 (6 H, s); λ_{max} (EtOH) 251 nm (ε 22900); mass spectrum m/e (rel. int.); 244 (0, M^+), 209 (17), 208 (100), 193 (40), 179 (18), 167 (26).

Anal.* Calcd. for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.48. Found: C, 78.73, 78.78; H, 7.18, 7.18; Cl, 14.00, 14.06.

Synthesis of 1-p-Biphenylyl-2-chloro-2-methylpropane

Methyl 2-p-Biphenylylacetate

This synthesis was via hydrolysis of the corresponding nitrile according to the general procedure given in "Organic Syntheses."[21] In a 1000-ml round-bottom flask were put 68.4 g (0.354 mole) of p-biphenylylacetonitrile and 350 ml of concentrated hydrochloric acid. Solution was heated at reflux with stirring for 48 hours and then filtered at room temperature. The solid collected was dissolved in ether and extracted with 10% KOH solution. The water layer was acidified with hydrochloric acid and filtered to give a yellow solid of crude

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[21]W. Wenner, Org. Syntheses, Coll. Vol. IV, John Wiley & Sons, Inc., New York (1963), p. 760.

p-biphenylylacetic acid. This acid was allowed to react with excess diazomethane and distilled. The distillate was collected at 136-140° and 0.05mmHg and amounted to 46.5 g (58%) of methyl p-biphenylylacetate: ^{1}H NMR ($CDCl_3$), δ 7.3-7.7 (9 H, m), 3.70 (3 H, s), 3.65 (2 H, s); literature[22] b.p. 140-143° at 0.5 mm.

1-p-Biphenylyl-2-methyl-2-propanol

This carbinol was synthesized in a 2000-ml Morton flask equipped with high-speed stirrer, addition funnel, and a condensor. To 23.3 g (0.960 g-atom) of magnesium and 300 ml of freshly distilled ether in the flask was added dropwise 40.0 ml (0.643 mole) of methyl iodide mixed with 250 ml of ether under a nitrogen atmosphere. After stirring for three hours, 46.5 g (0.205 mole) of methyl 2-p-biphenylylacetate in 350 ml of ether was added slowly. The solution was heated at reflux for 20 hours, and then 150 ml of a saturated ammonium chloride solution was added slowly at 0°. The organic layer was separated and washed once with water to give 43.1 g (93%) of crude product, m.p. 76-78°, which was recrystallized once from carbon tetrachloride to give needles m.p. 80-81°; λ_{max} (EtOH) 253 nm (ε 18900); ^{1}H NMR ($CDCl_3$); δ 7.3-7.8 (9 H, m), 2.80 (2 H, s), 1.51 (1 H, s), 1.25 (6 H, s); ^{13}C NMR ($CDCl_3$): δ 139.9 (s), 138.7 (s), 136.3 (s), 130.2 (d), 128.1 (d), 126.3 (d), 70.4 (s), 49.2 (t), 29.1 (q); mass spectrum m/e (rel. int.): 226 (2, M^+), 209 (2), 208 (8), 168 (100), 153 (7).

Anal.* Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.90 84.93; H, 8.03, 8.02.

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[22] L. F. Fieser, et al., J. Amer. Chem. Soc., 70, 3190 (1948).

*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

1-*p*-Biphenylyl-2-methyl-2-chloropropane

The conversion of 1-*p*-biphenylyl-2-methyl-2-propanol into 1-*p*-biphenylyl-2-methyl-2-chloropropane was first attempted by reacting 0.490 g (0.00217 mole) of the carbinol with 1.10 ml (0.0153 mole) of thionyl chloride in presence of 0.190 g (0.00240 mole) of pyridine at 0°. The product obtained contained 75% of the expected product and 25% of an olefin which according to its NMR spectrum, δ 6.26 (0.2 H, s), 1.96 (1.3 H, br s), was likely 1-*p*-biphenylyl-2-methyl-1-propene. In the second attempt, 0.408 g (1.80 mmole) of the carbinol was allowed to react with 3.00 ml (41.7 mmole) of thionyl chloride at 0°. The product had the same composition (NMR spectrum) as in the previous run. In the third run, 7.64 g (0.0338 mole) of the carbinol in 150 ml of carbon tetrachloride was allowed to react with 100 ml (1.39 mole) of thionyl chloride in 250 ml of chloroform at 0°. The product obtained contained 45% of olefin which was lowered to 21% by one recrystallization from hexane, and 7% by another recrystallization from cyclohexane (m.p. 94-95°). In the fourth run, 6.352 g (0.0281 mole) of the carbinol in 200 ml of chloroform was allowed to react with 9.00 ml (0.125 mole) of thionyl chloride at 0°. The product (6.42 g) contained only 10% of the undesired olefin which was lowered to 5% by one recrystallization from hexane. The product was sublimed and recrystallized from hexane to give the same composition (95% of 1-*p*-biphenylyl-2-methyl-2-chloropropane and 5% olefin). The pure analytical sample was finally obtained by HPLC of 0.75 g of the 95% pure sample through a 100-cm glass column (diameter 2.5 cm) filled with Merck-Darmstadt silica gel

60, with hexane-benzene (88/12) as eluant. The pure chloride (0.337 g) was recrystallized once from carbon tetrachloride to give 0.140 g of crystals with m.p. 97.0-97.5°; ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9 H, m), 3.11 (2 H, s), 1.60 (6 H, s); λ_{max} (EtOH) 252 nm (ε 22400); ^{13}C NMR: δ 140.1 (s), 139.0 (s), 135.3 (s), 130.5 (d), 128.1 (d), 126.0 (d), 125.9 (d), 69.5 (s), 51.2 (t), 32.0 (q); mass spectrum m/e (rel. int.); 244 (36, M^+), 209 (9), 208 (20), 193 (10), 167 (100).

Anal.* Calcd. for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.48. Found: C, 78.35; H, 7.10; Cl, 14.53

Synthesis of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane

2-p-Biphenylyl-2-propanol

The title compound was synthesized following the procedure of Mowry, et al.[23] Into 500-ml three-neck round-bottom flask equipped with a condensor, an addition funnel, and a mechanical stirrer was put 1.764 g (0.0726 g-atom) of magnesium under a nitrogen atmosphere. To the reaction flask was added dropwise 11.7 g (0.0821 mole) of methyl iodide in 40 ml of anhydrous ether. The solution was stirred for three hours and then 13.0 g (0.0663 mole) of phenylacetophenone in 200 ml of benzene was added dropwise at 0° during a period of 70 minutes. After stirring for ten hours, 200 ml of 3% sulfuric acid was added. The organic layer was separated, washed with water and 5% sodium bicarbonate,

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[23] D. T. Mowry, J. Dazzi, M. Renoll and R. W. Shortridge, J. Amer. Chem. Soc., 70, 1916 (1948).

and concentrated on a rotary evaporator to 12.6 g (90%) of crude product. Recrystallized twice from hexane, 7.82 g of crystals of m.p. 86.5-88.0° (literature[23] m.p. 92-93°). In another two runs, an average yield of 95% of crude product was obtained. The title compound was also synthesized by reacting p-biphenylylmagnesium bromide with acetone to give an average crude yield of 80%.

2-p-Biphenylyl-2-methoxypropane

An attempt to make tht title compound by reacting p-bromobiphenyl with lithium metal followed by addition of acetone and then methyl iodide failed; biphenyl was obtained as the only product. The title compound was finally made by reacting 4.35 g (0.0205 mole) of the corresponding carbinol in 50 ml of THF with 12.5 ml (0.0205 mole) of 1.67 N n-butyllithium at -75° followed by addition of 3.42 g (0.0241 mole) of methyl iodide at room temperature and then refluxing for 18 hours to give to give a mixture of 80% of the desired product and 20% of the unreacted carbinol. In another run, 41.6 g (0.196 mole) of the carbinol in 700 ml of THF was allowed to react with 170 ml (0.238 mole) of 1.67 N n-butyllithium at -75° for one hour; then, 68.4 g (0.482 mole) of methyl iodide in 200 ml of THF was added at room temperature. The solution was stirred at reflux for 22 hours to give, after work up, 43.0 g (0.190 mole, 96%) of the crude product. A portion of this product was distilled at 150° and 0.15 mm pressure to give only the decomposition product, 2-p-biphenylyl-1-propene. An attempt to transform 2-p-biphenylyl-1-propene into the desired product following the

procedure of Brown, et al.[24] by reacting the olefin with mercuric acetate and methanol failed. The crude methyl ether was used without further purification.

Methyl 2-p-Biphenylyl-2-methylpropanoate

This compound was synthesized by a general procedure of Gilman and Young.[25] Into a 500-ml Morton flask under a nitrogen atmosphere were put 6.00 g (0.177 mole) of Na-K alloy (containing 78% potassium, 0.120 g-atom, and 22% of sodium, 0.057 g-atom) and 175 ml of freshly distilled ether. A solution of 13.2 g (0.0584 mole) of 2-p-biphenylyl-2-methoxypropane in 50 ml of ether was added dropwise. The red solution was stirred for two hours after addition was finished, and then carbonated to give, after work up, 10.3 g (0.0429 mole, 73.3%) of crude 2-p-biphenylyl-2-methylpropanoic acid, which was recrystallized once from benzene and once from chloroform to give 6.96 g of crystals with m.p. 170.5-171.8°; ^{1}H NMR ($CDCl_3$); δ 8.78 (1 H, s), 7.2-7.7 (9 H, m), 1.59 (6 H, s).

In another run, 25.2 g (0.111 mole) of the starting ether was allowed to react with 11.9 g (0.352 g-atom) of Na-K alloy (containing 0.238 g-atom of K and 0.114 g-atom of Na). The solution was stirred for 90 minutes after addition was finished and then carbonated. The crude acid weighed 23.3 g (0.0971 mole, 86.8%).

Excess diazomethane generated from Diazald was added to the purified acid to give methyl 2-p-biphenylyl-2-methylpropanoate. This crude

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[24] H. C. Brown and M. H. Rei, J. Amer. Chem. Soc., 91, 5646 (1969).

[25] H. Gilman and H. Young, J. Org. Chem., 1, 315 (1936).

ester was sublimed and recrystallized once from n-pentane to give crystals of m.p. 70.5-71.5°; ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9 H, m), 3.69 (3 H, s), 1.61 (6 H, s); λ_{max} (EtOH) 251 nm (ε 22400); mass spectrum m/e (rel. int.): 254 (34, M^+), 195 (100), 181 (2), 167 (11), 153 (2).

Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.33, 80.29; H, 7.13, 7.15.

3-p-Biphenylyl-2,3-dimethyl-2-butanol

Attempts to synthesize the title compound by reacting 2-p-biphenylyl-2-methoxypropane with either potassium in ammonia (or ether) or lithium in ether, followed by addition of acetone, failed. The title compound was finally synthesized by allowing to react at reflux 20 hours 5.72 g (0.0225 mole) of methyl 2-p-biphenylyl-2-methylpropanoate with methylmagnesium iodide which was made from 1.16 g (0.0478 g-atom) of magnesium and 7.30 ml (0.117 mole) of methyl iodide in 55 ml of ether. The reaction mixture was decomposed with 70 ml of saturated ammonium chloride solution and after the usual work-up gave 6.16 g (0.0242 mole) of the crude product.

In another run, 15.0 g (0.0590 mole) of the starting ester in 200 ml of ether was allowed to react at reflux for 20 hours with the Grignard reagent made from 5.81 g (0.239 g-atom) of magnesium, 45.0 ml (0.723 mole) of methyl iodide, and 100 ml of ether. The crude carbinol isolated amounted to 15.2 g. This product was recrystallized from hexane and alcohol to give 11.4 g of crystals of m.p. 71-72°; ^{1}H NMR ($CDCl_3$):

δ 7.50 (9 H, m), 1.46 (6 H, s), 1.16 (6 H, s); λ_{max} (EtOH) 253 nm

(ε 21400); mass spectrum m/e (rel. int.): 254 (2, M^+), 237 (8), 236 (34), 196 (100), 195 (43), 167 (14); ^{13}C NMR ($CDCl_3$): δ 144.8 (s), 140.1 (s), 138.1 (s), 128.1 (d), 126.3 (d), 125.6 (d), 74.2 (s), 44.8 (s), 25.7 (q), 24.3 (q).

Anal.* Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.96, 84.93; H, 8.64, 8.65.

3-p-Biphenylyl-2-chloro-2,3-dimethylbutane

This compound was made by allowing to react 0.191 g (0.751 mmole) of the corresponding carbinol with 0.45 ml (6.24 mmole) of thionyl chloride in 5 ml of chloroform at room temperature to give 0.187 g (88.4%) of crude product. In another run, 0.495 g (1.942 mmole) of the carbinol and 1.15 ml (16.0 mmole) of thionyl chloride in 6 ml of chloroform were used to give 0.482 g (90.8%) of the crude chloride.

In a third run, 15.2 g (0.0597 mole) of the carbinol was allowed to react at room temperature for 10 hours and then at reflux for 90 minutes with 40.0 ml (0.556 mole) of thionyl chloride using 230 ml of chloroform as solvent to give 16.1 g (98.8%) of the product. The crude product was sublimed at 110° and 50 μ and recrystallized from hexane to give crystals of m.p. 110-111°; ^1H NMR ($CDCl_c$): δ 7.3-7.7 (9 H, m), 1.58 (6 H, s), 1.56 (6 H, s); λ_{max} (EtOH) 253 nm (ε 20900); mass spectrum m/e (rel. int.); 272 (0, M^+), 237 (20), 236 (100), 221 (90), 195 (77), 179 (35), 167 (25); ^{13}C NMR ($CDCl_3$): 143.3 (s), 140.0 (s), 138.3 (s), 128.4 (d), 128.1 (d), 126.3 (d), 125.2 (d), 77.2 (s), 45.8 (s), 29.3 (q), 25.2 (q).

*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

Anal.* Calcd, for $C_{18}H_{21}Cl$: C, 79.25; H, 7.76; Cl, 12.99. Found: C, 79.31, 79.30; H, 7.78, 7.76; Cl, 12.86, 12.87.

Synthesis of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)-2-butanol-1,1,1-d_3

3-p-Biphenylyl-3-methyl-2-(methyl-d_3)-2-butanol-1,1,1-d_3

This compound was synthesized following the same procedure as in making 3-p-biphenylyl-2,3-dimethyl-2-butanol by allowing to react for 20 hr. at reflux 21.0 g (0.0826 mole) of methyl 2-p-biphenylyl-2-methylpropanoate in 375 ml of ether with the Grignard reagent made from 5.49 g (0.226 g-atom) of magnesium and 24.9 g (0.172 mole) of methyl iodide-d_3, in 200 ml of ether. There was isolated 21.4 g (0.172 mole) of crude product which contained only 75% of the desired carbinol as shown by NMR. The unreacted methyl ester was removed by heating the product mixture with 40 g of potassium hydroxide in 1000 ml of ethanol for 12 hours, and then extracting it with ether to give 13.7 g of the carbinol which was sublimed and then recrystallized from carbon tetrachloride, to yield 8.4 g of crystals of m.p. 70-71°; ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9.0 H, m), 1.46 (5.9 H, s), 1.42 (1.0 H, s); mass spectrum m/e (rel. int.): 260 (0, M^+), 242 (11), 241 (17), 227 (4), 226 (13), 196 (100), 195 (39), 181 (68), 179 (9), 167 (15), 153 (4), 115 (4), 91 (3), 77 (5); ^{13}C NMR ($CDCl_3$): δ 144.8 (s), 140.1 (s), 138.1 (s), 128.1 (d), 128.0 (d), 126.4 (d), 125.6 (d), 73.9 (s), 44.7 (s), 24.3 (q).

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3

The title compound was synthesized by reacting 3-p-biphenylyl-3-methyl-2-(methyl-d_3)-2-butanol-1,1,1-d_3 with thionyl chloride at different conditions followed by decomposition with water; products were analyzed by the NMR spectra as listed in Table 1.

The last reaction was repeated by reacting 7.39 g (0.0284 mole) of the carbinol in 175 ml of carbon tetrachloride with a mixture of 2.28 g (0.0289 mole) of pyridine and 500 ml of thionyl chloride at 0°. After stirring for 5 days, the solution was poured into excess ice water and extracted with ether to give 6.84 g (0.0245 mole, 86.5%) of crude product, which contained 67% of 3-p-biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 and 33% of 3-p-biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3. This crude product was sublimed and recrystallized from hexane to give crystals of m.p. 109-110°; ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9.0 H, m), 1.58 (4.0 H, s), 1.56 (2.0 H, s): ^{13}C NMR ($CDCl_3$): in aliphatic region: δ 77.2 (s), 45.8 (s), 29.3 (q, peak height 9), 25.1 (q, peak height 19).

Synthesis of Methyl 4'-t-Butyl-4-biphenylcarboxylate

This compound was synthesized via Friedel-Craft reaction by reacting 5.93 g (0.0299 mole) of 4-biphenylcarboxylic acid with 2.80 g (0.0303 mole) of t-butyl chloride and 3.99 g (0.0299 mole) of aluminum chloride in carbon disulfide. After heating at reflux for three hours, solvent was evaporated, water was added and the mixture was extracted with ether to give 3.77 g of crude product containing 50% of the unreacted starting compound and 50% 4-(4'-t-butyl)biphenyl carboxylic

Table 1. Synthesis of 3-*p*-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3

Run	ROH (mmole)	Pyridine (mmole)	$SOCl_2$ (mmole)	Water (mmole)	Solvent	Temp. °C	Products%* I	II	III
1	0.442		11.1		4 ml $CHCl_3$	61	0	52	48
2	0.910	0.910	13.91		($SOCl_2$)	0	0	64	36
3	0.482	1.67	15.3	0.58	($SOCl_2$)	0	0	63	37
4	0.509	1.94	20.9	0.67	($SOCl_2$)	-78-0	0	54	46
5	0.511	0.510	1.67		pentane	-10	45	39	16
6	0.392	0.469	3.48		4 ml CCl_4	-10	73	20	7
7	0.449	0.598	5.56		$CHCl_3$	-10	0	63	37
8	0.394	0.446	27.8		($SOCl_2$)	-10	0	64	36
9	0.478	0.571	6.95		5 ml THF + 0.9 ml $CHCl_3$	0	69	24	7
10	0.556	0.611	6.95		5 ml CS_2 + 10 ml $CHCl_3$	0	32	53	14
11	0.392		6.95		6 ml CS_2	0	0	50	50
12	0.480		6.95		5 ml THF	0	80	16	4
13	0.376		6.95		5 ml THF	0-65	70	20	10
14	0.351	0.391	6.95		5 ml $CHCl_3$ + 2 ml CS_2	0	41	41	17
15	0.376	0.401	6.95		4.5 ml $CHCl_3$ 2 ml CCl_4	0	27	51	22
16	0.292	0.341	48.7		($SOCl_2$)	0	13	55	32
17	0.337	0.456	55.6		($SOCl_2$)	0	20	53	27
18	0.356	0.374	55.6		4 ml $CHCl_3$ + 4 ml $SOCl_2$	0	22	50	27
19	0.773	(with 2.95 mmole $Bu(Me)_3NCl$ in 60 ml HCl + 30 ml $CHCl_3$)				25	73	12	15
20	0.418	0.421	139.0		2.5 ml CCl_4 + 10 ml $SOCl_2$	0	0	66	33

*I. Starting carbinol.
II. Title product.
III. Rearranged product.

acid as analyzed by G. C. as methyl ester. The pure analytical sample was collected on G. C. as methyl ester and recrystallized from hexane to give needles with m.p. 130.0-130.5°; ^{1}H NMR ($CDCl_3$); δ 7.4-8.2 (8 H, m) 3.96 (3 H, s), 1.40 (9 H, s); λ_{max} (EtOH): 281 nm (ε 12600): mass spectrum m/e (rel. int.): 268 (37, M^+), 253 (100), 237 (12), 225 (17), 181 (12).

Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.61, 80.60; H, 7.52, 7.53.

Synthesis of Methyl 4'-t-Butyl-3-biphenylcarboxylate

3-Biphenylcarboxylic acid

This compound was synthesized following a general procedure given in "Organic Syntheses."[26] 3-Methylbiphenyl, 5.48 g (0.0326 mole), was allowed to react with 17.1 g (0.108 mole) of potassium permanganate in 200 ml of water. The solution was heated at reflux for 10 hours and then filtered while hot. The filtrate was acidified with hydrochloric acid and extracted with ether. The ethereal layer was extracted with 5% KOH solution; the alkaline extract was acidified and extracted again with ether to give 1.33 g of crude 3-biphenylcarboxylic acid which after recrystallization from alcohol had m.p. 164-165°, (literature[27] m.p. 167-168°); ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9 H, m), 10.6 (1 H, s).

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[26]H. T. Clarke and E. R. Taylor, Org. Syn., Col. Vol. II, 135 (1955).

[27]G. F. Woods, P. H. Griswold, Jr., B. H. Armbrecht and D. I. Blumenthal, J. Amer. Chem. Soc., 71, 2030 (1949).

Methyl 4'-t-Butyl03Obiphenylcarboxylate

This compound was synthesized via the Friedel-Craft reaction by reacting 0.820 g (0.00411 mole) of 3-biphenylcarboxylic acid with 0.385 g (0.00416 mole) of t-butyl chloride and 0.535 g (0.00401 mole) of aluminum chloride in carbon disulfide at reflux for 2 hours, there resulted 0.735 g of crude product which still contained about one-third of the unreacted starting acid by G. C. analysis. The crude product was transformed to methyl ester by adding excess diazomethane and collected on G. C. to give pure methyl 4'-t-butyl-3-biphenylcarboxylate, after one recrystallization from hexane, the compound had m.p. 77.5-78.5°; ^{1}H NMR ($CDCl_3$); δ 7.4-8.4 (8 H, m with sharp s at 7.61), 3.98 (3 H, s), 1.40 (9 H, s); λ_{max} (EtOH) 205 nm (ε 20,610), 236 nm (ε 16,600), 255 nm (sh, ε 10,600); mass spectrum m/e (rel. int.): 268 (62, M^+), 253 (100), 237 (14), 225 (23), 181 (42), 165 (16).

Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.52, 80.49; H, 7.51, 7.50.

Synthesis of 2-(4-cyclohexylphenyl)-2,3-dimethylbutane

This compound was synthesized by hydrogenation of 2-p-biphenylyl-2,3-dimethylbutane. To a 300 ml three-neck round-bottom flask was put 100 ml of tetrahydrofuran and 2.22 g (0.0567 g-atom) of potassium. Solution was heated to reflux until potassium was molten. To this solution was added a mixture of 0.663 g (0.00278 mole) of the starting hydrocarbon and 4.96 g (0.0669 mole) of t-butyl alcohol. The solution was

*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

stirred at reflux for 10 hours until all the potassium was reacted, water added and the mixture was extracted with ether to give 0.678 g of crude product. The product on simple distillation gave a pure sample of b.p. (70 μ) 100°; ^{1}H NMR ($CDCl_3$): δ 7.20 (4 H, AB quart, J = 8.4 Hz, Δν = 9.1 Hz), 1.4-2.2 (12 H, m), 1.24 (6 H, s), 0.75 (6 H, d, J = 6.4 Hz); λ_{max} (EtOH) 251 nm (ε 307), 256 (312), 262 (293), 272 (213); mass spectrum m/e (rel. int.): 244 (2, M^+), 201 (100), 187 (4), 173 (5), 159 (8), 145 (11).

Anal.* Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.39, 88.42; H, 11.60, 11.56.

Reaction of 3-p-Biphenylyl-1-chloropropane with Cs-K-Na Alloy

For run one, into a 500-ml Morton flask containing 250 ml of freshly distilled tetrahydrofuran was put 5.57 g (0.0419 g-atom) of cesium, 1.88 g (0.0481 g-atom) of potassium, and 0.289 g (0.0126 g-atom) of sodium,[28] and the mixture was stirred at reflux for one hour. The final blue solution was cooled to -75° and 1.28 g (0.00554 mole) of the starting chloride in 25 ml of dry THF was added during a period of two minutes to form initially a deep red solution which turned to green in one minute. The solution was stirred at -75° for another 8 minutes and then carbonated. The usual work up yielded 0.263 g of neutral

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[28]The eutectic composition of Cs-K-Na alloy, cf: F. Tepper, J. Knig, and J. Greer, The Alkali Metals, An International Symposium Held at Nottingham on 14-22nd July, 1966, The Chemical Society, 1967, p. 25.

material and 0.912 g of acid. The neutral material on simple distillation gave 0.222 g of a clear oil with b.p. (0.09 mm) 102°; ^{1}H NMR ($CDCl_3$): δ 7.2-7.7 (9 H, m), 2.65 (2 H, t, J = 7 Hz), 1.64 (2 H, sextet, J = 7 Hz), 0.96 (3 H, t, J = 7 Hz); mass spectrum, molecular ion m/e 196; identified to be n-propylbiphenyl, literature b.p. 296°.[41] The acidic product which was quantitatively analyzed by G. C. as methyl ester contained 0.42% of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (III), 2.0% of 4-p-biphenylylbutanoic acid (IV), 6.5% of 2-p-biphenylylbutanoic acid (V), and 5.8% of p-biphenylyl-acetic acid (VI) (all listed as molar % yield based on starting chloride), and 0.46 g of non-volatile acids. Acids V, VI and IV were identified by comparisons of G. C. retention times and mass spectra with authentic samples synthesized. Synthesis of VI was reported somewhere else. Acid V was synthesized by reacting p-biphenylylacetonitrile with K in liquid ammonia at -33° followed by addition of bromoethane at room temperature to give 2-p-biphenylyl-2-ethylacetonitrile which was hydrolyzed with sulfuric acid to give acid V, after recrystallization from hexane to give crystals with m.p. 120-121°; ^{1}H NMR ($CDCl_3$); δ 11.4 (1 H, s), 7.2-7.7 (9 H, m), 3.51 (1 H, t, J = 7 Hz), 2.00 (2 H, octet, J = 7 Hz), 0.92 (3 H, t, J = 7 Hz); mass spectrum, M^+ m/e 240; literature m.p. 123-125°.[42] Acid IV was made by Dr. S. Akabori.[5]

In run two, Cs-K-Na alloy from 6.22 g (0.0468 g-atom) of Cs, 1.94 g (0.0496 g-atom) of K, and 0.286 g (0.0124 g-atom) of Na in 250 ml of THF

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[41] I. A. Romadane and S. E. Berga, Zhur. Obshchei, Khim., 28, 413 (1958).

[42] F. F. Blicke and N. Grier, J. Amer. Chem. Soc., 65, 1727 (1943).

was prepared as above. A solution of 3.04g (0.0132 mole) of the chloride in 15 ml of THF was added at -75° over a period of two minutes. The color of the solution changed from the original blue to yellow, red, purple and then, black in two minutes. The solution was stirred for another 40 seconds after addition had been finished, and then 4.4 ml (60 g, 0.30 g-atom) of mercury was added as a very fine stream during a period of 4.5 minutes. About half of the black solution was carbonated to give 0.616 g of acid and 0.197 g of neutral material. The rest of the solution was warmed up to -30 to -40°, stirred for ten minutes, and finally carbonated to give 1.01 g of acid and 0.362 g of neutral material. Quantitative G. C. analyses of the first fraction gave 24.2% of n-propylbiphenyl, 0.20% of p-methylbiphenyl, 8.2% of p-biphenylylacetic acid, 12.4% of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid, 3.9% of 2-p-biphenylylbutanoic acid and 1.5% of 4-p-biphenylylbutanoic acid, and 0.30 g of nonvolatile acids; and the second fraction gave 7.3% of p-biphenylylacetic acid, 11.1% of 2-p-biphenylylbutanoic acid, 0.12% of 4-p-biphenylylbutanoic acid, 28% of n-propylbiphenyl, 0.90% of p-methylbiphenyl, and no spiro acid (all listed as molar % yield based on starting chloride), and 0.61 g of non-volatile acids.

In run three, 2.53 g (0.0110 mole) of the chloride in 25 ml of THF was added at -75° over a period of 12 seconds to a solution of 250 ml of THF containing CS-K-Na alloy made from as usual 5.56 g (0.0418 g-atom) of Cs, 1.81 g (0.0463 g-atom) of K and 0.298 g (0.0129 g-atom) of Na. The solution was stirred for another 21 seconds and carbonated, to give 1.82 g of acid and 0.678 g of neutral material. Quantitative G. C. analyses gave 23.0% (molar yield based on starting chloride) of

n-propylbiphenyl, 0.80% of p-methylbiphenyl, 35.8% of 7-phenylspiro-[3.5]nona-5,8-diene-7-carboxylic acid, 13.8% p-biphenylacetic acid, 2.6% of 2-p-biphenylylbutanoic acid, 6.0% of 4-p-biphenylylbutanoic acid, and 0.53 g of non-volatile acids.

The acidic product 1.8 g, from run three was separated by liquid chromatography through a glass column (1 meter in length and 25 mm diameter) packed with 240 g of silica gel (Merch 70-325 mesh, ASTM, 0.05-0.20 mm), using ether-cyclohexane-benzene (20/40/40) as eluant. The major acid isolated was 0.185 g of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid as light yellow crystals, which were recrystallized twice from hexane to give 0.100 g of acid of m.p. 130.5-131.5°; ^{1}H NMR ($CDCl_3$): δ 10.4 (1.0 H, s), 7.31 (5.0 H, s), 6.09 (4.0 H, AB quartet, J = 10.2 Hz, $\Delta\nu$ = 11 Hz), 2.08 (6.0 H, s); λ_{max} (EtOH) 259 nm (ε 1039), 262 (1132), 265 (1184), 269 (1250), 279 (1211); mass spectrum m/e (rel. int.): 240 (2, M^+), 211 (4), 195 (7), 179 (2), 167 (100), 153 (7).

Anal.* Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.96, 79.86; H, 6.73, 6.77.

In run four, 2.73 g (0.0118 mole) of the chloride in 13 ml of THF was added at -75° over a period of 12 seconds to 250 ml of THF containing Cs-K-Na alloy made from 6.00 g (0.0451 g-atom) of Cs, 1.66 g (0.0424 g-atom) of K, and 0.315 g (0.0137 g-atom) of Na. The solution was carbonated in fractions after stirring for another 25 seconds, 59 seconds, 118 seconds, and 175 seconds respectively (ave. reaction time: 38 sec.,

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

66 sec., 121 sec., 182 sec.). After the usual work up, the first fraction gave 0.568 g of acid which was analyzed by quantitative G. C. as methyl ester to contain 18.0% (molar yield based on starting chloride) of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (III), 6.8% of p-biphenylylacetic acid (VI), 2.0% of 2-p-biphenylylbutanoic acid (V), 5.0% of 4-p-biphenylylbutanoic acid (IV), and 0.21 g of non-volatile acids, and 0.116 g of neutral material containing 0.10 g (13%) of n-propylbiphenyl (II). The second fraction contained 0.590 g of acid which on G. C. analyses showed 17.9% of III, 6.8% of VI, 2.2% of V, 4.7% of IV and 0.29 g of non-volatile acids, and 0.110 g of the neutral material containing 13% (based on chloride) of n-propylbiphenyl. The third fraction contained 0.592 g of acid consisting of 16.2% of III, 6.6% of VI, 3.0% of V, 4.7% of IV, and 0.30 g of non-volatile acids, and 0.126 g of neutral material containing 14% (based on chloride) of II. The fourth fraction contained 0.141 g of acid consisting of 12.7% of III, 6.4% of VI, 4.2% of IV and 0.090 g of non-volatile acids, and 0.031 g of neutral material containing 14% (based on chloride) of II.

In run five, to 250 ml THF in a Morton flask containing Cs-K-Na alloy made from 5.72 g (0.0430 g-atom) of Cs, 1.87 g (0.0479 g-atom) of K, and 0.332 g (0.0145 g-atom) of Na was added 2.90 g (0.0126 mole) of the chloride in 15 ml of THF over a period of 11.5 seconds at -75°. The solution was fractionally carbonated after stirring for another 26 sec., 295 sec., 594 sec., and 903 sec. (ave. reaction time: 35 sec., 304 sec., 603 sec., 912 sec. respectively). After usual work up, the first fraction gave 0.248 g of acid which contained by quantitative G. C.

19.3% (molar yield based on starting chloride) of 7-phenylspiro[3.5]-nona-5,8-diene-7-carboxylic acid (III), 8.7% of p-biphenylylacetic acid (VI), 2.3% of 2-p-biphenylylbutanoic acid (V), 1.9% of 4-p-biphenylyl-butanoic acid (IV), and 0.088 g of non-volatile acids, and 0.734 g of neutral material which by quantitative G. C. analysis contained 52% of unreacted chloride and 11.4% of n-propylbiphenyl. The second fraction gave 0.546 g of acid consisting of 12.1% of III, 5.2% of VI, 3.1% of V, 0.5% of IV, and 0.250 g of non-volatile acids, and 0.222 g of neutral material as only II. The third fraction gave 0.312 g of acid consisting of 9.4% of III, 4.1% of VI, 0.6% of IV, 4.1% of V, and 0.18 g of non-volatile acids, and 0.116 g of neutral material II. The fourth fraction gave 0.222 g of acid consisting 7.1% of III, 3.5% of VI, 4.5% of V, 0.1% of IV, and 0.14 g of non-volatile acids, and 0.105 g of neutral material II.

In run six, 7.31 g (0.0276 mole) of 18-crown-6 was added to 200 ml of THF at -75° containing the Cs-K-Na alloy made from 5.47 g (0.0411 g-atom) of Cs, 1.68 g (0.0430 g-atom) of K, and 0.299 g (0.0130 g-atom) of Na. After stirring for 20 minutes, 2.72 g (0.0118 mole) of the chloride in 12 ml of THF was added during a period of 34 seconds and then the solution was immediately carbonated to give, after work up, 0.571 g of neutral material which according to quantitative G. C. was 18% (based on chloride) of n-propylbiphenyl, and 2.34 g of acid. Quantitative G. C. analysis of the acidic product as methyl ester gave 9.1% (molar yield based on starting chloride) of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid, 4.64% of p-biphenylylacetic acid, 9.26%

of 2-p-biphenylylbutanoic acid, and 1.24 g of non-volatile acids.

In run 7, 10.8 g (0.0410 mole) of 18-crown-6 and 6.18 g premade Cs-K-Na alloy (containing 0.0334 g-atom of Cs, 0.0384 g-atom of K and 0.0104 g-atom of Na) in 250 ml of THF were used. A solution of 1.62 g (0.00701 mole) of the chloride in 15 ml of THF was added at -75° during a period of 13 seconds. After stirring for another 12 seconds, solution was carbonated to give, after work up, 0.276 g of neutral material, primarily n-propylbiphenyl, and 1.28 g of acid. Quantitative G. C. analysis gave 12.3% (molar yield based on starting chloride) of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid, 3.0% of p-biphenylylacetic acid, 10.4% of 2-p-biphenylylbutanoic acid, 0.3% of 4-p-biphenylylbutanoic acid, and 0.64 g of non-volatile acids.

In run 8, 6.13 g (0.0818 g-atom) of premade Cs-K-Na alloy (containing 40.3 atom % of Cs, 47.3 atom % of K, and 12.3 atom % of Na) in 250 ml of diethyl ether was used. Reaction was first tried at -75° by adding 7 drops of the chloride solution (total chloride used, 2.39 g, 0.0104 mole in 17 ml of ether) to the reaction flask. After stirring for 20 minutes, there was no sign of reaction. The solution was heated to reflux, and then the rest of the chloride solution was added over a period of 7 minutes with stirring continued for another 6 minutes. Then, 136 g (0.678 g-atom) of mercury was added over a period of 5.5 minutes. After another minute's stirring, half of the solution was carbonated. The rest of the solution was carbonated after another 5 minutes' stirring. After work up, the first fraction gave 0.863 g of neutral material containing 82% of unreacted chloride and 11% of

n-propylbiphenyl and 0.0288 g of acid containing 0.03% of p-biphenylylacetic acid (all yields listed as molar yield based on starting chloride). The second fraction gave 0.728 g of neutral material containing 72.6% of unreacted chloride and 12% of n-propylbiphenyl, and 0.0110 g of acid containing 0.02% of p-biphenylylacetic acid, 0.01% of 2-p-biphenylylbutanoic acid and 0.01% of 4-p-biphenylylbutanoic acid.

In run 9, 6.03 g (0.0804 total g-atom) of premade Cs-K-Na alloy (containing 40.3 atom % of Cs, 47.3 atom % of K, 12.3 atom % of Na) in 210 ml of 2-methyltetrahydrofuran (MTHF) was used. A solution of 1.74 g (0.00752 mole) of the chloride in 11 ml of MTHF was added at -75° during a period of 9 seconds. The color of the solution changed from the original blue to yellow, red, then green in total 34 seconds of stirring, and then the solution was carbonated during a period of 35 seconds. The average reaction time was 63 seconds. After work up, were obtained 0.393 g of neutral material, chiefly n-propylbiphenyl, and 1.23 g of acid containing 19.5% (molar % yield based on starting chloride) of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid and 1.3% of p-biphenylylacetic acid. The acidic product was sublimed and the first fraction collected, 0.190 g, was recrystallized from cyclohexane to give crystals of m.p. 106.5-108.0°, with ^{1}H NMR ($CDCl_3$): δ 11.4 (1 H, s), 7.28 (1 H, d, J = 3 Hz), 6.16 (1 H, d, J = 3 Hz), 2.38 (3 H, s); identified to be 2-methylfuran-5-carboxylic acid, literature[29] m.p. 108-109°. The second fraction collected, 0.290 g,

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[29]W. R. Kirner and G. H. Richter, J. Amer. Chem. Soc., 51, 3134 (1929).

was identified as 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid. The methyl esters of these two acids had the same retention time on G.C. under the conditions used.

Reaction of 3-p-Biphenylylpropyllithium with Potassium t-Butoxide

In the first run, 2.98 g (0.429 g-atom) of lithium cut into small pieces was put into 200 ml of tetrahydrofuran in a 500 ml Morton flask under a nitrogen atmosphere. Methyl iodide. 0.10 ml (1.6 mmole) was added at -15° and solution was stirred at this temperature for 30 minutes. A solution of 3.20 g (0.0139 mole) of 3-p-biphenyl-1-chloropropane in 20 ml of THF was added during a period of 15 minutes at -75°. The color of the solution changed from red to green after another 20 minutes' stirring. Two 2-ml samples were withdrawn for double Gilman titration to give 0.0323 mole (due to over reduction) of organolithium compound in solution. All the solution was transferred to an adjacent Morton flask to separate the solution from lithium metal, and 20 ml (1.35 g-atom) of mercury was added. After stirring at -25° for 25 minutes, the color of the solution turned back to red. The first portion of the solution was carbonated to give 0.088 g of neutral material, mostly n-propylbiphenyl (II) by G. C., and 0.122 g of acid which according to quantitative G.C. analysis of the methyl esters contained 2.1% (molar yield based on starting chloride) of 2-p-biphenylylbutanoic acid (V), 23.8% of 4-p-biphenylylbutanoic acid (IV). The rest of the solution was cooled to -75° and to it was added 100 ml of cold potassium t-butoxide solution (0.27 N, by titration with standard acid) made from 3.20 g (0.0818 g-atom) of K and

and 4.75 g (0.0641 mole) of t-butanol in 250 ml of THF. A second portion of the solution was carbonated 30 seconds after mixing to give 0.053 g of neutral material (largely II), and 0.084 g of acid which by G. C. contained 6.3% of V and 17.2% of IV. The third portion carbonated 10 minutes after mixing gave 0.063 g of neutral material (mainly II) and 0.0903 g of acid containing 7.8% of V, 13.7% of IV, 2.5% of p-biphenylylacetic acid (VI), and 0.045 g of non-volatile acids. The fourth portion carbonated 20 minutes after mixing gave 0.059 g of neutral material II, and 0.0775 g of acid containing 7.7% V, 12.7% IV, 2.4% VI, and 0.038 g of non-volatile acids. The fifth portion carbonated 30 minutes after mixing gave 0.189 g of neutral material II, and 0.230 g of acid containing 9.4% of V, 11.8% of IV, 2.7% of VI, and 0.095 g of non-volatile acids. The sixth fraction carbonated 50 minutes from mixing gave 0.486 g of neutral material (mainly II) and 0.595 g of acid containing 8.9% of V, 10.9% of IV, 2.6% of VI, and 0.27 g of non-volatile acids.

In the second run 1.94 g (0.280 g-atom) of lithium in 250 ml of THF was allowed to react with 1.62 g (0.00701 mole) of the chloride at -75°. A portion of the organolithium solution was carbonated to give 0.0444 g of neutral material which according to NMR and G. C. was n-propylbiphenyl (II) and 0.0446 g of acid which by quantitative G. C. of the methyl esters contained 31.2% (molar yield based on starting chloride) of 4-p-biphenylylbutanoic acid (IV). To the rest of the solution was added 100 ml of the t-BuOK solution (0.25 N. by titration with standard acid, 0.025 mole of t-BuOK was added here) made by reacting 3.52 g (0.0899

g-atom) of K with 4.76 g (0.0642 mole) of t-butanol in 250 ml of THF. The second fraction of the reaction solution was carbonated 50 seconds after mixing, to give 0.0487 g of neutral material, mainly II, and 0.0176 g of acid which contained 0.86% of 2-p-biphenylylbutanoic acid (V), 7.9% of IV, 0.18% of p-biphenylylacetic acid (VI). The third fraction was carbonated 8.5 minutes after mixing and contained 0.317 g of neutral material, chiefly II, and 0.0937 g of acid composed of 2.3% of V, 7.2% of IV and 0.63% of VI. The fourth fraction carbonated 19 minutes after mixing gave 0.297 g of neutral material (chiefly II), and 0.084 g of acid containing 3.1% of V, 5.4% of IV and 0.8% of VI. The rest of the solution carbonated 28 minutes after mixing gave 0.281 g of neutral material, mostly II, and 0.072 g of acid containing 3.6% of V, 4.5% of IV and 0.6% of VI.

Reaction of 3-p-Biphenylyl-1-propyllithium with Cesium t-Butoxide

Cesium t-butoxide solution was made by reacting 5.65 g (0.0425 g-atom) of Cs with 2.49 g (0.0336 mole) of t-butanol in 200 ml of THF under a nitrogen atmosphere in a dry box for three hours. Five ml aliquots upon titration with standard acid gave a concentration of 0.121 N.

The organolithium compound was made as usual by adding 0.2 ml of methyl iodide and 10 drops of the chloride solution (1.12 g, 0.00486 mole of 3-p-biphenylyl-1-chloropropane in 15 ml of THF) to 250 ml of THF containing 1.17 g (0.169 g-atom) of lithium at -10°. After stirring for another 43 minutes, the color of the solution turned from red to

purple. A portion of the solution was carbonated to give, after work up, 0.135 g of neutral material, which by G. C. analysis was n-propylbiphenyl, and 0.140 g of acid which was analyzed by quantitative G.C. as methyl ester to contain 27.2 mole % yield of 4-p-biphenylylbutanoic acid (IV) based on starting chloride. To the rest of the solution was added 80 ml (0.00968 mole) of t-BuOCs. A second fraction was carbonated 2 minutes after adding the t-BuOCs solution to give 0.144 g of neutral material (n-propylbiphenyl by G.C.) and 0.0777 g of acid. Quantitative G.C. analyses of the acid gave 0.4% of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (III), 3.6% of IV and 6.7% of 2-p-biphenylylbutanoic acid (V). The third fraction carbonated 10 minutes after mixing gave 0.175 g of neutral material (n-propylbiphenyl) and 0.0952 g of acid which by quantitative G. C. contained 0.1% of III, 3.1% of IV and 9.0% of V. The fourth fraction carbonated 18 minutes after mixing, gave 0.241 g of neutral material (n-propylbiphenyl) and 0.128 g of acid which contained 2.6% of IV, and 9.7% of V.

Reaction of 2-p-Biphenylyl-1-chloroethane[7] with Cs-K-Na Alloy

This reaction was carried out under the usual conditions in a 500-ml Morton flask under a nitrogen atmosphere with 220 ml of freshly distilled THF as solvent. Into the flask was put 5.08 g (0.0382 g-atom) of Cs, 1.97 g (0.0503 g-atom) of K, and 0.269 g (0.0117 g-atom) of Na. The mixture was heated at reflux with rapid stirring for one hour, and then was cooled to -75°. A solution of 1.98 g (0.00916 mole) of 2-p-biphenylyl-1-chloroethane in 20 ml of THF was added during a period of

22 seconds. The deep red solution was carbonated after stirring for another 28 seconds. The usual work up yielded 0.726 g of acid and 1.06 g of neutral material. G. C. analyses of the acid as methyl ester and the neutral material gave 3.6% of 3-p-biphenylyl-propanoic acid, 2.2% of 2-p-biphenylylpropanoic acid, 38% of unreacted chloride, 27% of ethylbiphenyl, with less than 1% of 6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (if there was any) (all yields listed as mole % yield based on starting chloride).

Reaction of 2-p-Biphenylyl-1-chloro-2-methyl-propane with Cs-K-Na Alloy

In run 1, into 500 ml Morton flask containing 220 ml of freshly distilled tetrahydrofuran was put 5.87 g (0.0784 total g-atom) of Cs-K-Na alloy (containing 40.3 atom % of Cs, 47.3 atom % of K, 12.3 atom % of Na). The solution was stirred at room temperature for 30 minutes and then at -75° for another 30 minutes. To this cold solution was added a solution of 2.50 g (0.0102 mole) of 2-p-biphenylyl-1-chloro-2-methylpropane in 13 ml of THF during a period of 17 seconds. The color of the solution changed to yellow, red, then green within another minute of stirring. Half of the solution was carbonated to give, after work up, 0.950 g of neutral material, which according to G. C. was mainly t-butylbiphenyl (XII), and 1.06 g of acid, which was analyzed by quantitative G. C. as methyl ester to contain 18.8% of 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII), 2.7% of 3-p-biphenylyl-3-methylbutanoic acid (IX), 2.2% of 4'-t-butyl-3-biphenylcarboxylic acid (X) and 6.4% of 4-p-biphenylyl-3-methyl-3-butenoic acid (XI). The neutral product on simple distillation

gave 0.80 g of a clear liquid with b.p. (0.1 mm) 108°; ^{1}H NMR ($CDCl_3$): δ 7.2-7.7 (9H, m), 1.34 (9 H, s); mass spectrum, M^+ m/e 210; identified to be t-butylbiphenyl, literature b.p. 310°.[41] The second half of the solution was carbonated after standing for 200 seconds to give 0.129 g of neutral material which was essentially t-butylbiphenyl by G. C., and 0.173 g of acid which by G. C. contained 14.1% of VIII, 1.1% of IX, 0.5% of X and 2.5% of XI.

In run 2, 2.50 g (0.0102 mole) of the chloride in 16 ml of THF was added to 250 ml of THF in a 500-ml Morton flask containing 5.74 g (0.0766 total g-atom) of Cs-K-Na alloy (same composition as in run 1) at -75° during a period of 11 seconds. After stirring for another 47 seconds, half of the solution was carbonated to give 0.371 g of neutral material, which by G. C. analysis was mainly t-butyl-biphenyl (XII), and 0.416 g of acid. Quantitative G. C. analyses of this acidic product as methyl ester gave 20.2% of 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII), 1.82% of 3-p-biphenylyl-3-methylbutanoic acid (IX), 3.0% of 4'-t-butyl-3-biphenylcarboxylic acid (X) and 12.0% of 4-p-biphenylyl-3-methyl-3-butenoic acid (XI). To the rest of the solution was added 5.2 ml (0.351 g-atom) of mercury as a very fine stream with stirring over a period of 2.2 minutes. The solution was carbonated after total 10 minutes of stirring to give 0.428 g of neutral material (mainly XII by G. C.) and 0.997 g of acid which by quantitative G. C. contained (based on starting chloride used for this fraction of the reaction) 13.9 mole % VIII, 0.83 mole % IX, 2.2 mole % X, and 8.9 mole % XI.

The methyl ester from the first fraction of acidic product from

this run, 0.26 g, was separated by liquid chromatography through a 120-cm glass column (3.6 cm diameter) packed with 240 g of Merck-Darmstadt silica gel (0.05-0.20 mm, 70-325 mesh ASTM, packing height 51 cm). Eluant was collected in 100 ml fractions. Nothing was collected in fractions 1-17 (hexane as eluant), 18-34 (hexane-benzene (75/25) as eluant), 35-51 (hexane-benzene (50/50) as eluant). Finally hexane-benzene (5/95) was used. Fractions 54-55 gave 80 mg of crystals which on simple distillation gave 75 mg of a mixture identified by NMR spectrum to be 9% of X and 91% of a compound with ^{1}H NMR ($CDCl_3$): δ 7.42 (9 H, m), 4.96 (2 H, d, J = 5.5 Hz), 4.36 (1 H, s), 3.66 (3 H, s), 1.75 (3 H, s); mass spectrum of the sample collected on preparative G. C., m/e (rel. int.): 266 (53, M^+), 207 (100), 195 (16), 191 (23), 179 (61), 165 (51); ^{13}C NMR: δ 171.7 (s), 142.1 (s), 140.3 (s), 139.8 (s), 135.5 (s), 128.7 (d), 128.3 (d), 126.7 (d), 113.6 (t), 58.3 (d), 51.8 (q), 21.7 (q); suggested to be 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII). Fraction 56 gave 45 mg of a mixture of 20% of VIII and 80% of a compound with ^{1}H NMR: δ 7.2-7-7 (9 H, m), 6.52 (1 H, s), 3.73 (3 H, s), 3.28 (2 H, s), 2.00 (3 H, d, J = 0.5 Hz), and mass spectrum of a sample collected on preparative G. C., M^+ m/e 266, suggested to be 4-p-biphenylyl-3-methyl-3-butenoic acid (XI). Fractions 57-58 gave 30 mg of a mixture containing 15% of XI and 85% of 4'-t-butyl-3-biphenylcarboxylic acid (X) identified by comparisons of G. C. retention time, NMR spectrum and mass spectrum with authentic synthetic sample. Fraction 60 gave 10 mg of 3-p-biphenylyl-3-methylbutanoic acid (IX) identified by comparisons of G. C. retention time mass spectrum and NMR spectrum

with known sample.

In run 3, 2.11 g (0.00863 mole) of the chloride in 17 ml of THF was added to the flask containing 250 ml of THF and 5.12 g (0.0674 g-atom) of eutectic Cs-K-Na alloy at -75° during a period of 740 seconds. After stirring for another 20 seconds, the solution was carbonated. There was obtained, after the usual work-up, 0.993 g of neutral material (by G. C. analysis mainly t-butyl-biphenyl) and 0.866 g of acid. G. C. analysis of the acidic product as methyl esters gave (area %) 25.1% of 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII), 2.4% of 3-p-biphenylyl-3-methyl-butanoic acid (IX), 10% of 4'-t-butyl-3-biphenyl-carboxylic acid (X), and 31% of 4-p-biphenylyl-3-methyl-3-butenoic acid (XI).

Reaction of 2-p-Biphenylyl-1-chloro-2-methylpropane with Cs-K-Na Alloy in Presence of Methanol

To a 500 ml Morton flask containing 250 ml of freshly distilled tetrahydrofuran was put 5.96 g (0.0797 total g-atom) of Cs-K-Na alloy (containing 0.0319 g-atom of Cs, 0.0389 g-atom of K and 0.00895 g-atom of Na) under a nitrogen atmosphere. The solution was stirred at room temperature for 30 minutes and then at -75° for another 30 minutes. A solution of 1.08 g (0.00439 mole) of the chloride in 18 ml of THF mixed with 1.10 ml (0.0272 mole) of MeOH was added during a period of 16 seconds. The color of the solution soon changed from the original blue to yellow and then light green. The solution was stirred for another 40 seconds and then syphoned out onto excess crushed dry ice. The product after the usual work-up consisted of 0.804 g of neutral material.

Quantitative G.C. analyses gave 54.4 mole % of 1-t-butyl-4-cyclohexylbenzene (XVII), 6.6 mole % of 1-s-butyl-4-cyclohexylbenzene (XVIII), 5.9 mole % of t-butyl-biphenyl (XII), and 2.3 mole % of s-butylbiphenyl (XIII). Compounds XVII and XVIII were identified by comparisons of G. C. retention times and the mass spectra of the samples collected on preparative G.C. with authentic synthetic samples. Compounds XII and XIII were identified by comparisons of G.C. retention time and the mass spectra of samples collected on preparative G.C. with known samples. Compound XVII, synthesized by reduction of t-butyl-biphenyl with K in presence of t-BuOH at reflux for 4 hr., had b.p. 88° at 90 μ (literature[40] b.p. 333-340°); ^{1}H NMR ($CDCl_3$): δ 7.20 (4 H, q), 1.31 (9 H, s) 0.8-1.9 (11 H, m); mass spectra m/e (rel. int.): 216 (40, M^+), 201 (100), 173 (11), 160 (7), 117 (20). Compound XVIII, synthesized by reduction of s-butylbiphenyl with K in presence of t-BuOH at reflux for 12 hours, had b.p. 89-90° at 110 μ (literature[40] b.p. 142-144° at 8 mm pressure); ^{1}H NMR ($CDCl_3$): δ 7.1-7.3 (4 H, m, with sharp s at 7.10), 2.45 (2 H, d, J = 7 Hz), 1.2-2.1 (12 H, m), 0.89 (6 H, d, J = 6 Hz); mass spectrum m/e (rel. int.): 216 (74, M^+), 173 (100), 159 (10), 131 (9), 117 (54).

Reaction of 2-p-Biphenylyl-1-chloro-2-methylpropane with Lithium

In run 1, into a 500 ml Morton flask was distilled 230 ml of tetrahydrofuran and then 1.25 g (0.179 g-atom) of lithium which cut into small pieces was added. The solution was cooled to -5 to -10° and 0.12 ml of methyl iodide and 15 drops of the chloride solution (totally 1.43

[40] S. V. Zavgorodnii, I. A. Nasyr, I. N. Novikov, and E. V. Alisova, Ukr. Khim. Zh., 35, 374 (1969).

g, 0.00586 mole of the chloride in 18 ml of THF) were added. After stirring for 40 minutes, a pink color developed. The solution was cooled to -75°. The rest of the chloride solution was added during a period of 13 minutes. After stirring for another 11 minutes, the color of the solution turned from red to green, then, the solution was carbonated. After usual work up there were obtained 0.447 g of neutral material which according to G. C. analysis consisted of a 96 to 4 ratio of t-butylbiphenyl to s-butylbiphenyl, and 0.981 g of acid which by G. C. and NMR spectral analyses of its methyl ester contained only two volatile components, 3-p-biphenylyl-3-methylbutanoic acid (IX) and 3-p-biphenylyl-2,2-dimethylpropanoic acid (XIV) in a ratio of 87/13 respectively. Acid XIV was identified by comparisons of G. C. retention time and mass spectrum of the sample collected on preparative G. C. with an isolated pure known sample whose full characterization is given elsewhere.

3-p-Biphenylyl-3-methylbutanoic acid was isolated by high pressure liquid chromatography through a one meter glass column (2.6-cm diameter) filled with Merck-Darmstadt silica gel 60 using ether-cyclohexane (30/70) as eluant. The acid isolated after recrystallization from hexane had m.p. 122.0-123.2°; ^{1}H NMR ($CDCl_3$): δ 10.3 (1 H, s), 7.3-7.7 (9 H, m), 2.69 (2 H, s), 1.50 (6 H, s); λ_{max} (EtOH) 252 nm (ε 15500); mass spectrum m/e (rel. int.): 254 (28, M^+), 195 (100), 179 (9), 167 (10); ^{13}C NMR ($CDCl_3$): δ 177.3 (s), 146.4 (s), 140.2 (s), 138.2 (s), 128.1 (d), 126.3 (d), 125.2 (d), 47.7 (t), 36.6 (s), 28.7 (q).

Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.27, 80.31; H, 7.15, 7.17.

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

In run 2, 1.45 g (0.00592 mole) of the chloride was allowed to react with 1.24 g (0.179 g-atom) of lithium in 250 ml of THF at -75°. After stirring for 80 minutes, the color of the solution turned from red to green. Fifty ml of the solution was withdrawn by a syringe and carbonated to give, after work up, 0.150 g of neutral material, which by quantitative G.C., contained 37.9 mole % of t-butylbiphenyl (XII) and 1.6 mole % of s-butylbiphenyl (XIII), and 0.161 g of acid, which by quantitative G.C. contained 40.0 mole % of 3-p-biphenylyl-3-methylbutanoic acid (IX) and 7.1 mole % of 3-p-biphenylyl-2,2-dimethylpropanoic acid (XIV). To the remaining solution in the Morton flask was added 4 ml (0.27 g-atom) of mercury as a very fine stream while stirring rapidly, then the solution was warmed up to -20°. After stirring at this temperature for 60 minutes, 100 ml of the solution was carbonated, to give 0.339 g of neutral material which by quantitative G. C. contained 51.7 mole % of XII and 2.2 mole % of XIII, and 0.203 g of acid, which by quantitative G. C. analysis contained 31.4 mole % of IX and 1.7 mole % of XIV. The rest of the solution in the flask was warmed up to 0° by an ice bath. Another 16 ml of mercury was added. After stirring at 0 to 5° for two hours, the solution was carbonated to give 0.511 g of neutral material which by quantitative G. C. analysis contained 80.5 mole % of XII and 3.5 mole % of XIII, and no acid. The yield for each fraction which was carbonated are based on the starting alkyl chloride which was estimated to have been present in the fraction based on the weights of neutral and acidic material isolated.

In run 3, 1.08 g (0.00440 mole) of the chloride in 15 ml of THF was reacted with 1.13 g (0.162 g-atom) of lithium. Reaction was initiated

by stirring 10 drops of the chloride solution and 0.25 ml of methyl iodide with lithium in 250 ml of THF at -10° for 50 minutes to give a pink color. The solution was cooled to -75°, and all the chloride solution was added. After stirring for 65 minutes, the color of the solution turned from red to green. Half of the solution was then carbonated to give, after work up, 0.197 g of neutral material which according to quantitative G. C. analysis contained 30.1 mole % yield of t-butylbiphenyl (XII) and 1.2 mole % of s-butylbiphenyl (XIII), and 0.202 g of acid, which contained 3.7 mole % of 3-p-biphenylyl-2,2-dimethylpropanoic acid (XIV) and 28.1 mole % of 3-p-biphenylyl-3-methylbutanoic acid (IX). The rest of the solution was kept at -75° for another 120 minutes and carbonated to give 0.333 g of neutral material containing 33.2 mole % XII and 3.1 mole % of XIII, and 0.265 g of acid containing 17.6 mole % of IX and 1.8 mole % of XIV.

Reaction of 2-p-Biphenylyl-1-chloro-2-methylpropane with Lithium in Presence of t-BuOH

In run one, 2.08 g (0.300 g-atom) of lithium cut into small pieces was put into a 500-ml Morton flask containing 250 ml of freshly distilled tetrahydrofuran. To this solution was added 15 drops of the chloride solution (totally 1.92 g, 0.00783 mole of the chloride in 15 ml of THF) and 0.1 ml of methyl iodide at -10°. After stirring for 50 minutes, the solution turned to a pink color. The solution was then cooled to -75° and the chloride solution together with 1.76 g (0.0237 mole) of t-BuOH were added rapidly. A red color developed in one minute

but disappeared on longer stirring. The solution was stirred for one hour and then syphoned out onto excess crushed Dry Ice. The usual work-up gave 1.45 g of neutral material which by quantitative G. C. contained 48.0 mole % of t-butylbiphenyl, 5.8 mole % of s-butylbiphenyl and 28.7 mole % of starting chloride.

In run two, 3.26 g (0.470 g-atom) of lithium was used. The reaction was initiated at -75° by adding 15 drops of the chloride solution (totally 2.58 g, 0.01056 mole of the chloride in 15 ml of THF) and 0.3 ml of methyl iodide with lithium. After stirring for three hours, there was still no sign of reaction. To this solution was added 1.0 ml of 2.5 N n-butyllithium solution. A pink color developed in 5 minutes. The rest of the chloride solution together with 3.23 g (0.0436 mole) of t-BuOH was added slowly. After stirring for 25 minutes, the color of the solution turned slightly green. The solution was syphoned onto excess crushed Dry Ice. The usual work-up gave 2.25 g of neutral material containing 19.7 mole % yield of 1-t-butyl-4-cyclohexylbenzene, 3.4 mole % of 1-s-butyl-4-cyclohexylbenzene, 30.5 mole % of t-butylbiphenyl and 7.4 mole % of s-butylbiphenyl by quantitative G. C. analysis. Structure of each product was confirmed by mass spectrum of each sample collected on preparative G. C.

Reaction of 2-p-Biphenylyl-2-methyl-1-propyllithium with Potassium t-Butoxide

In run one, two sets of experimental apparatus were set up side by side in the hood each with a 500-ml Morton flask, high-speed stirrer, reflux condensor and addition funnel under a nitrogen atmosphere. Into

each flask, 250 ml of THF was distilled from $NaAlH_4$. To the first flask was added 4.69 g (0.120 g-atom) of potassium. The solution was heated at reflux with rapid stirring for 30 minutes; then 7.03 g (0.0949 mole) of t-butanol in 12 ml of THF was added dropwise. After the addition was finished, the solution was stirred for two hours at reflux, and cooled to room temperature. An aliquot of this t-BuOK solution was withdrawn and titrated with 0.050 N triphenylmethyllithium solution. The unreacted alcohol was found to be 15%. This t-BuOK solution was heated to reflux again for another two hours. An aliquot was withdrawn and titrated with triphenylmethyllithium to give only 4% of unreacted alcohol.

Into the second flask was put 0.181 g (0.0260 g-atom) of lithium. After stirring at -10° for 15 minutes, 0.1 ml of methyl iodide and 10 drops of the chloride solution (totally 2.05 g, 0.00839 mole of 2-p-biphenylyl-1-chloro-2-methylpropane in 16 ml of THF) were added and the solution was stirred for 40 minutes. Since there was no sign of reaction, to the solution was added 1.5 ml (0.00368 mole) of 2.45 N n-butyllithium solution and 0.1 ml of methyl iodide. After stirring for 25 minutes, a pink color formed. The solution was cooled to -75°. All the chloride solution was added over a period of 4 minutes. The solution was stirred for 3 hours to give a bright red solution. A portion of this solution was carbonated to give, after work-up, 0.191 g of neutral material (only t-butylbiphenyl was revealed by G. C. analysis), and 0.258 g of acid containing 3-p-biphenylyl-3-methylbutanoic acid (IX) and 3-p-biphenylyl-2,2-dimethylpropanoic acid (XIV) in a ratio of 88 : 12.

To the second flask was added 120 ml of t-BuOK solution from the first flask. The solution was stirred for 40 seconds, and the second portion was carbonated after 70 seconds of mixing to give 0.193 g of neutral material, containing by G. C. analysis 20 mole % of unreacted chloride and 25 mole % of t-butylbiphenyl (XII), and 0.070 g of acid containing by G. C. analysis 6.0 mole % of an acid suspected to be 4-t-butyl-3-carboxylic acid (XVI), 5.1 mole % of 3-p-biphenylyl-3-methylbutanoic acid (IX), 5.6 mole % of 4'-t-butyl-3-biphenylcarboxylic acid (X), and 4.1 % of 4'-t-butyl-4-biphenylcarboxylic acid (XV) with relative retention time 0.93, 1.00, 1.30, 1.36 respectively.

The third portion of solution was carbonated after 5 minutes of mixing to give 0.236 g of neutral material identified by G. C. as t-butylbiphenyl, and 0.085 g of acid containing 2.6 mole % of IX, 4.5 mole % of X, 3.0 mole % of XV and 4.5 mole % of suspected XVI. The fourth portion was carbonated after 10 minutes of mixing to give 0.219 g of neutral material XII and 0.080 g of acid identified as 2.2 mole % of IX, 3.5 mole % of X, 2.5 mole % of XV and 3.0 mole % of suspected XVI. The fifth portion of solution was carbonated after 20 minutes of mixing to give 0.432 g of neutral material (primarily XII), and 0.148 g of acid identified as 2.0 mole % of IX, 3.2 mole % of X, 2.2 mole % of XV and 2.4 mole % of suspected XVI. The sixth portion of solution was carbonated after 30 minutes of mixing to give 0.195 g of neutral material XII, and 0.068 g of acid identified as 1.2 mole % of IX, 2.4 mole % of X, 1.5 mole % of XV and 2.0 mole % of suspected XVI.

In run two, 5.23 g (0.134 g-atom) of K and 7.50 g (0.101 mole) of

t-BuOH were used to make t-BuOK. The final t-BuOK solution contained about 1.2 % of unreacted t-BuOH according to titration with standard triphenylmethyllithium solution. The organolithium was made by reacting 1.94 g (0.00794 mole) of the chloride with 1.386 g (0.200 g-atom) of lithium at -75°. Half of the organolithium solution was carbonated to give, after work up, 0.084 g of neutral material containing 4 mole % of unreacted chloride and 36 mole % of t-butylbiphenyl (XII), and 0.122 g of acid containing 3-p-biphenylyl-3-methylbutanoic acid (IX) and 3-p-biphenylyl-2,2-dimethylbutanoic acid (XIV) in a ratio of 86 : 14 respectively.

To the rest of the organolithium solution was added 75 ml (0.0330 mole) of t-BuOK solution. The solution was stirred for 30 seconds and stood without stirring for another 10 minutes before carbonated. The product after the usual work up gave 1.28 g of neutral material (mainly t-butylbiphenyl) and 0.400 g of acid containing relative yield of 19.4% of a compound suspected to be 4-t-butylbiphenyl-3-carboxylic acid, 19% of 3-p-biphenylyl-3-methylbutanoic acid, 38% of 4'-t-butyl-3-biphenylcarboxylic acid, and 17% of 4'-t-butyl-4-biphenylcarboxylic acid. The methyl ester of the second fraction of acidic products, 0.40 g, was separated by liquid chromatography through a 100 cm long (3.6 cm diameter) glass column packed with 220 g of Merck-Darmstadt silica gel (70-325 mesh ASTM) with benzene as solvent. Eluant was collected in 50 ml fractions. Fractions 7-9 gave 20 mg of a compound with ^{1}H NMR: δ 7.50 (9 H, m), 3.92 (3 H, s), 1.44 (9 H, s); suggested to be 4-t-butylbiphenyl-3-carboxylic acid (XVI). Fractions 10-12 gave 100 mg of

a mixture containing 75% of 4'-t-butyl-3-biphenylcarboxylic acid (X) and 25% of XVI by NMR analysis. Fractions 13-17 gave 38 mg of crystals by NMR as 95% of 4'-t-butyl-4-biphenylcarboxylic acid (XV). Fractions 18-20 gave 30 mg of a sample containing 95% of 3-p-biphenylyl-3-methylbutanoic acid (IX) and 5% of XV by NMR analysis. Compounds X, XV, and IX were also identified by the mass spectra of each compound collected on preparative G. C.

Reaction of 1-p-Biphenylyl-2-chloro-2-methylpropane with Cs-K-Na Alloy

The self-synthesized chloride containing 95% mole of 1-p-biphenylyl-2-chloro-2-methylpropane and 5% of 1-p-biphenylyl-2-methyl-1-propene was used in all the reactions of this compound. The reaction was run as usual using a 500-ml Morton flask equipped with high-speed stirrer, condensor and addition funnel under a nitrogen atmosphere.

In run one, 6.59 g of Cs-K-Na alloy (containing 0.0361 g-atom of Cs, 0.0396 g-atom of K and 0.0122 g-atom of Na) was added to a flask containing 230 ml of freshly distilled THF. The solution was stirred at room temperature for 30 minutes, and then at -75° for another 30 minutes. To this cold solution was added 0.735 g (2.87 mmole) of 1-p-biphenylyl-2-chloro-2-methylpropane in 17 ml of THF during a period of 23 seconds. The color of the solution turned to deep red immediately. After stirring for another 277 seconds, the red solution was carbonated. After work up, there were obtained 0.537 g of neutral material (containing by quantitative G. C. as 35.7 mole % of unreacted chloride, 4.6 mole % yield of s-butylbiphenyl and 23.9 mole % yield of t-butylbiphenyl) and 0.106 g

of acid. Quantitative G. C. analyses of the acid as methyl ester gave 2.24 mole % yield of 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII), 0.57 mole % of 3-p-biphenylyl-3-methyl-butanoic acid (IX) and 3.14 mole % of 4-p-biphenylyl-3-methyl-3-butenoic acid (XI). Compounds VIII, IX, and XI were identified by comparisons of G. C. retention time, NMR spectra of the crude product, and mass spectra of each compound collected on preparative G. C., with products isolated from reaction of 2-p-biphenylyl-1-chloro-2-methylpropane with Cs-K-Na alloy.

In run two, 5.99 g of Cs-K-Na alloy (containing 0.0328 g-atom of Cs, 0.0360 g-atom of K and 0.0111 g-atom of Na) was allowed to react with 0.596 g (0.00233 mole) of the chloride at -75°. The addition of the chloride solution took 62 seconds. The solution was stirred for another 10 seconds and then carbonated, to give 0.222 g of neutral material (containing by quantitative G. C. analysis 27.1 mole % yield of t-butylbiphenyl and 6.1 mole % of s-butylbiphenyl) and 0.391 g of acid (containing 1.21 mole % yield of 2-p-biphenylyl-3-methyl-3-butenoic acid, 0.25 mole % of 3-p-biphenylyl-3-methylbutanoic acid, and 0.60 mole % of 4-p-biphenylyl-3-methyl-3-butenoic acid).

In run three 0.849 g (3.321 mmole) of the chloride was allowed to react with 5.44 g of Cs-K-Na alloy (containing 29.8 mg-atom of Cs, 2.7 mg-atom of K and 10.1 mg-atom of Na). The addition of the chloride solution took 12 seconds. After stirring for another 38 seconds, the solution was carbonated to give, after work up, 0.396 g of neutral material and 0.439 g of acid. Quantitative G. C., analyses gave 33 mole % yield of t-butylbiphenyl, 9.5 mole % of s-butylbiphenyl, 4.8 mole % of 2-p-biphenylyl-3-methyl-3-butenoic acid, 0.4 mole % of 3-p-biphenylyl-3-methylbutanoic acid, and 4.0 mole % of 4-p-biphenylyl-3-methyl-3-

butenoic acid together with some 3% of diacids identified by mass spectra (parent peak 326).

Reaction of 1-p-Biphenylyl-2-chloro-2-methylpropane with Cs-K-Na Alloy in Presence of Methanol

This reaction was run as usual under a nitrogen atmosphere using 500-ml Morton flask containing 225 ml of freshly distilled THF and equipped with high-speed stirrer, addition funnel, and condensor. To the THF was added 4.42 g of Cs-K-Na alloy (containing 0.0242 g-atoms of Cs, 0.0266 g-atom of K, and 0.0082 g-atom of Na). The solution was stirred at room temperature for 30 minutes, and then at -75° for another 20 minutes. To this cold solution was added a solution of 0.639 g (2.615 mmole) of the chloride in 15 ml of THF mixed with 1.00 ml (24.7 mmole) of methanol during a period of 15 seconds. The color of the solution changed from deep blue to yellow, then slightly green. After stirring for another 25 seconds, the solution was carbonated. After the usual work up, there was obtained 0.573 g of neutral material containing by quantitative G. C. 19.4 mole % yield of 1-t-butyl-4-cyclohexylbenzene (XVII), 38.7 mole % of 1-s-butyl-4-cyclohexylbenzene (XVIII), 1.26 mole % of t-butylbiphenyl, and 2.7 mole % of s-butylbiphenyl. Compound XVII and XVIII were identified by comparisons of G. C. retention time, NMR and mass spectra with authentic samples synthesized.

Reaction of 1-p-Biphenylyl-2-chloro-2-methylpropane with Lithium

Into a 500-ml Morton flask was distilled 250 ml of THF, and then

1.23 g (0.177 g-atom) of lithium cut into small pieces was added. The solution was cooled to -10°. To the solution were added 0.2 ml of methyl iodide and 10 drops of the chloride solution (totally 0.783 g, 0.00322 mole of the chloride in 16 ml of THF). After stirring for 22 minutes, a pink color developed. The solution was cooled to -75° and the rest of the chloride solution was added rapidly. After stirring for 35 minutes after addition had been complete the color of the solution turned to deep purple. This solution was carbonated to give, after work up, 0.352 g of neutral material and 0.441 g of acid. Quantitative G. C. analyses showed the presence of 29.5 mole % yield of 3-p-biphenylyl-2,2-dimethylpropanoic acid (XIV), 7.4 mole % of 3-p-biphenylyl-3-methylbutanoic acid (IX), 18.8 mole % of t-butylbiphenyl and 23.8 mole % of s-butylbiphenyl.

The acidic product 0.40 g was separated through a glass column with inner diameter 2.6 cm and length 100 cm, filled with EM grade silica gel 60, with cyclohexane-ether (70:30) as eluant. Fractions of 25 ml size were collected. Fractions 33-48 gave only XIV. Fractions 49-54 gave mixture of XIV and IX. Compound IX was identified by comparisons of G. C. retention time and NMR spectrum with known sample. Fractions 33-48 were combined, dissolved in ether, extracted with 5 % KOH solution, the water layer acidified with HCl and extracted with ether again to give 0.133 g of white crystals. These were recrystallized once from CCl_4 to give pure compound XIV with m.p. 148-149°; ^{1}H NMR ($CDCl_3$): δ 10.4 (1 H, s), 7.2-7.6 (9 H, m), 2.93 (2 H, s), 1.23 (6 H, s); λ_{max} (EtOH) 253 nm (ε 20,900); ^{13}C NMR ($CDCl_3$): δ 183.5 (s),

140.3 (s), 138.9 (s), 136.0 (s), 130.1 (d), 128.1 (d), 126.4 (d), 44.5 (t), 43.3 (s), 24.7 (q); mass spectrum m/e (rel. int.): 254 (11, M^+), 240 (1), 209 (1), 195 (4), 167 (100), 153 (3).

Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.26, 80.23; H, 7.13, 7.15

The neutral product, 0.33 g, was separated through the same column with hexane as eluant. Fractions of 25 ml size were collected. Fractions 12-14 gave 90 mg of t-butylbiphenyl (XII) identified by NMR, mass spectrum and G. C. retention time. Fractions 15-16 gave 70 mg of a mixture of XII and s-butylbiphenyl (XIII). Fractions 17-19 gave 110 mg of s-butylbiphenyl which was distilled to have b.p. 94° at 0.1 mm with ^{1}H NMR: δ 7.2-7.7 (9 H, m), 2.54 (2 H, d, J = 7 Hz), 1.74 (1 H, m), 0.91 (6 H, d, J = 7 Hz), literature b.p. 282-286°.[43]

This reaction was repeated by using 0.512 g (1.984 mmole) of the chloride to react with 0.815 g (0.117 g-atom) of lithium. The first fraction was carbonated after stirring at -75° for 40 minutes, to give 0.131 g of neutral material and 0.065 g of acid. Quantitative G. C. analysis showed the presence of 17.7 mole % yield of t-butylbiphenyl, 18.4 mole % of s-butylbiphenyl, 16.9 mole % of 3-p-biphenyl-2,2-dimethylpropanoic acid (XIV) and 3.3 mole % of 3-p-biphenylyl-3-methylbutanoic acid (IX). The composition of XIV and IX in the acidic product was confirmed by mass spectrum of this mixture which was recrystallized once from hexane with no change of composition. The mass spectrum gave major

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*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

[43] I. Romadane and T. I. Rendel, J. Gen. Chem. USSR, 26, 215 (1956).

m/e (rel. int.) at 195 (11) and 167 (100). The rest of the solution was kept at -75° for another 3 hours without stirring and then carbonated to give 0.233 g of neutral material and 0.073 g of acid. Quantitative G. C. analysis gave 18.1 mole % yield of t-butylbiphenyl, 30.4 % of s-butylbiphenyl, 5.3 mole % of XIV, and 0.6 mole % of IX.

Reaction of 1-p-Biphenylyl-2-chloro-2-methylpropane with Lithium in Presence of t-BuOH

This reaction was run using a 500-ml Morton flask, equipped with high-speed stirrer, addition funnel, and condensor. To 250 ml of freshly distilled THF was added 1.31 g (0.189 g-atom) of lithium which was cut into small pieces. The solution was stirred at -75° for 30 minutes and then 0.30 ml (4.8 mmole) of methyl iodide and 2.0 ml of 2.5 N n-butyllithium solution were added. After stirring for 15 minutes, 0.806 g (0.00329 mole) of the chloride in 18 ml of THF mixed with 3.38 g (0.0456 mole) of t-BuOH was added rapidly. After stirring for 3 hours at -75°, a slightly green color appeared. The solution was syphoned onto excess freshly crushed Dry Ice. Excess lithium was destroyed by adding excess MeOH. After work-up, 0.674 g of neutral material was obtained. Quantitative G. C. analysis gave 13.0 mole % yield of 1-t-butyl-4-cyclohexylbenzene, 27.1 mole % of 1-s-butyl-4-cyclohexylbenzene, 2.77 mole % of t-butylbiphenyl, and 27.2 mole % of s-butylbiphenyl. These products were identified by comparisons of G. C. retention times and mass spectra of each compound collected on preparative G. C. with known samples.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Lithium

These reactions were run as usual using a 500-ml Morton flask containing 250 ml of freshly distilled THF and equipped with a high-speed stirrer, addition funnel, and condensor under a nitrogen atmosphere.

In run one, 0.803 g (0.120 g-atom) of lithium and 0.730 g (2.68 mmole) of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane in 20 ml of THF were used. Lithium cut into small pieces was added to the flask. The reaction mixture was cooled to -10° with stirring. To the reaction mixture were added 1.0 ml (16 mmole) of methyl iodide and 10 drops of the chloride solution. After stirring for 80 minutes, a pink color appeared. The solution was cooled to -75°. All the rest of the chloride solution was added dropwise during a period of 3 minutes. The color of the solution turned to deep red in 15 minutes. After stirring for a total of 50 minutes, the solution was carbonated to give, after work up, 0.448 g of neutral material (containing by quantitative G. C. analysis 6.3 mole % yield of 3-p-biphenylyl-2,3-dimethyl-1-butene, 1.9 mole % of unreacted chloride, and 41.0 mole % yield of 2-p-biphenyl-2,3-dimethylbutane) and 0.321 g of acid (containing 37 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid. The acidic product was recrystallized from CCl_4 to give pure 3-p-biphenylyl-2,2,3-trimethylbutanoic acid, m.p. 208-209°; ^{1}H NMR ($CDCl_3$): δ 10.4 (1.0 H, s), 7.3-7.7 (9.0 H, m), 1.53 (6.0 H, s), 1.14 (6.0 H, s); λ_{max} (EtOH) 253 nm (ε 21,200); mass spectrum m/e (rel. int.): 282 (2, M^+), 249 (3), 221 (3), 195 (100), 181 (8), 167 (20), 153 (6); ^{13}C NMR ($CDCl_3$) δ 176.8 (s), 144.4 (s), 139.4 (s),

137.0 (s), 128.1 (d), 127.7 (d), 126.4 (d), 125.8 (d), 124.7 (d), 47.6 (s), 37.9 (s), 25.0 (q), 22.1 (q).

Anal.* Calcd. for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.63, 80.62; H, 7.89, 7.87.

The neutral products were separated by liquid chromatography through a 90-cm long glass column (diameter 2.3 cm) packed with 100 g of Merck-Darmstadt silica gel (75-200 mesh) with packing height 55 cm, using cyclohexane as eluant. Pure 2-p-biphenylyl-2,3-dimethylbutane was collected with ^{1}H NMR ($CDCl_3$) δ 7.2-7.7 (9.0 H, m), 1.55-2.10 (1.0 H, septet, J = 7 Hz), 1.24 (6.0 H, s), 0.80 (6.0 H, d, J = 7 Hz); b.p. (0.04 mm) 116-117°; λ_{max}(EtOH) 252 nm (ε 20,480); mass spectrum m/e (rel. int.): 238 (9, M^+), 223 (1), 195 (100), 167 (9), 153 (2).

Anal.* Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.76, 90.75; H, 9.24, 9.22.

A fraction of impure 3-p-biphenylyl-2,3-dimethyl-1-butene was also collected with ^{1}H NMR ($CDCl_3$): δ 7.2-7.7 (9 H, m), 4.96 (1 H, s), 5.00 (1 H, s), 1.58 (3 H, s), 1.49 (6 H, s). A sample of it was collected on prep G. C. which had mass spectrum m/e (rel. int.): 236 (11, M^+), 221 (4), 195 (100), 181 (2), 167 (5).

In run two, 0.912 g (3.34 mmole) of the chloride was allowed to react with 0.947 g (0.136 g-atom) of lithium at -75° in the usual manner. After stirring for 50 minutes, half of the solution was carbonated to give, after work-up, 0.190 g of acid containing 34.2 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX) and 0.186 g of neutral

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material containing 9.6 mole % recovery of unreacted chloride, 22.1 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane (XXII), and 8.7 mole % of 3-p-biphenylyl-2,3-dimethyl-1-butene (XXVI). The rest of the solution was kept at -75° for another 150 minutes without stirring, and then carbonated to give, after work-up, 0.201 g of acid containing 19.1 mole % yield of XX and 0.427 g of neutral material containing 4.0 mole % recovery of chloride, 40.8 mole % yield of XXII and 10.0 mole % of XXVI.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Lithium Biphenylide

The reaction was run under a nitrogen atmosphere using a 500-ml Morton flask containing 230 ml of freshly distilled THF and equipped with a high-speed stirrer, addition funnel, and reflux condensor. Into the flask were put 0.837 g (0.121 g-atom) of lithium and 1.5 ml (24 mmole) of methyl iodide. The solution was stirred for 15 minutes at room temperature. To this solution was slowly added 6.65 g (43.1 mmole) of biphenyl in 20 ml of THF at room temperature. After stirring for 5 minutes, a blue color developed. The solution was cooled to -75° and stirred for three hours. By double Gilman titration, the solution contained 17.8 mmole of organolithium compound. A solution of 0.807 g (2.96 mmole) of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane in 20 ml of THF was added over a period of 7 minutes, followed by dropwise addition of 2.5 ml (23.9 mmole) of n-butyl chloride, and then the solution was carbonated, to give 0.585 g of acid (containing valeric acid) and 6.22 g of neutral material (containing biphenyl). Quantitative G. C.

analyses gave 4 mole % recovery of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane, 32 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane and 28 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid.

Reaction of 2-p-Biphenylyl-1.1.2-trimethylpropyllithium with CsO-t-Bu

The CsO-t-Bu solution was made by reacting 6.59 g (0.0496 g-atom) of Cs with 2.23 g (0.0301 mole) of t-BuOH in 230 ml of THF at reflux for two and one half hours. A 5-ml aliquot of the solution was withdrawn and titrated with standard acid to give a normality of 0.114 N.

The organolithium compound was made as usual by reacting 1.06 g (0.00389 mole) of 3-p-biphenylyl-2,3-dimethyl-2-chlorobutane in 20 ml of THF with 1.42 g (0.204 g-atom) of lithium at -75° in 250 ml of THF. The reaction was initiated by adding 15 drops of the chloride solution and 0.2 ml of methyl iodide at -10°. After stirring for 25 minutes, a pink color developed. Solution was cooled to -75°. All the rest of the chloride solution was added. After stirring for 36 minutes, the color of the solution changed from deep red to blackish red. A portion of the solution was withdrawn and carbonated, to yield 0.122 g of acid, which by quantitative G. C. contained 33.4 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid, and 0.117 g of neutral material which by G. C. contained 9.4 mole % recovery of chloride and 28.9 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane. To the rest of the organolithium solution was added 80 ml (0.00915 mole) of the CsO-t-Bu solution which was pre-cooled to -75°. The resulting solution was stirred for 5 minutes

and a portion of it was carbonated to give, after work-up, 0.197 g of neutral material (containing by quantitative G. C. analysis 9.1 mole % recovery of chloride and 32.3 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, and 0.115 g of acid (20.8 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXI), and 8.4 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX)). The rest of the solution was carbonated after standing for another 12 minutes. The usual work up yielded 0.352 g of neutral material containing 8.7 mole % recovery of chloride and 34.6 mole % yield of XXII, and 0.209 g of acid containing 16.6 mole % yield of XXI and 7.1 mole % yield of XX.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy

The reaction was run as usual using 250 ml of freshly distilled THF as solvent in a 500-ml Morton flask equipped with addition funnel, reflux condensor, and high-speed stirrer in a dry box.

In run one, to the flask was put 6.01 g (0.0791 g-atom) of Cs-K-Na alloy (containing 41.1 atom % of Cs, 48.4 atom % of K, and 10.5 atom % of Na). The solution was stirred at room temp. for 30 minutes and then at -75° for 20 minutes. A solution of 0.811 g (2.97 mmole) of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane in 20 ml of THF was added during a period of 13 seconds to form a deep red color solution. After stirring for another 31 seconds, the color changed to green. Solution was carbonated. The usual work-up, gave 0.305 g of neutral material and 0.525 g of acid. Quantitative G. C. analyses of the acid as methyl ester

and the neutral material gave 27.7 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, 6.8 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid, 0.95 mole % recovery of chloride, and 32.3 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane.

In run two, 5.66 g (0.0745 g-atom) of the Cs-K-Na alloy (same composition as in run 1) was allowed to react with 1.40 g (0.00512 mole) of the chloride at -75°. The chloride solution was added during a period of 12 seconds. After stirring for another 28 seconds, the solution was carbonated to give 0.507 g of neutral material and 0.979 g of acid. Quantitative G. C. analyses gave 0.85 mole % recovery of unreacted chloride, 30.3 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, 26.2 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid and 7.31 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid.

The acidic products of the above two runs were combined for a total of 1.28 g of acid which was separated by liquid chromatography through a 120-cm glass column (3.6 cm diameter) packed with 235 g of Merck-Darmstadt silica gel (0.05-0.20 mm) to give a packing height of 50 cm, with hexane-ether used as eluant. The first component collected using hexane-ether (60/40) as eluant, was 0.294 g of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid, identified by comparisons of G. C. retention time, NMR spectrum, and mass spectrum, and by mixed m.p. with a known sample. The second component using hexane-ether (20/80) as eluant, was 0.266 g of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-

carboxylic acid.* The latter compound was recrystallized twice from benzene-hexane to give crystals of m.p. 182-183° (some decomposition at 163°); ^{1}H NMR ($CDCl_3$): δ 10.6 (1 H, s, CO_2H), 7.34 (5 H, br s, phenyl), 6.01 (4 H, AB quartet, J = 11.0 Hz, Δν = 20.4 Hz, vinyl), 1.19 and 1.14 (12 H, overlapping s, methyl); λ_{max} (EtOH) 269 nm (sh, ε 377), 218 (21,900); mass spectrum m/e (rel. int.): 282 (5, M^+), 267 (1), 238 (20), 237 (41), 221 (7), 195 (21), 181 (100), 167 (22), 152 (12); ^{13}C NMR ($CDCl_3$): δ 173.7 (s, C15), 144.4 (s, C11), 128.4, 127.5, and 126.4 (all d, vinyl and phenyl C), 53.5 (s, C6), 32.7, 32.5, and 32.1 (all s, cyclopropyl C), 19.2 and 19.0 (both q, methyl C). (Carbon assignments see Figure 14).

Anal.** Calcd. for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.67, 80.60; H, 7.85, 7.86.

The structure of this acid was also determined independently by single-crystal x-ray diffraction analysis. (See Appendix A.)

In run three, 6.25 g (0.0823 g-atom) of Cs-K-Na alloy (same composition as in run one) was allowed to react with 0.971 g (0.00356 mole) of the chloride in 250 ml of THF at -75°. The chloride solution was added to the flask during a period of 13 seconds. After stirring for four and one half minutes, the first fraction of the solution was carbonated to give, after work up, 0.0530 g of acid and 0.171 g of neutral material. These by quantitative G. C. analysis contained 6.2 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-

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*Only about half of this acid survived chromatography on this grade of silica gel.

**Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

carboxylic acid (XXI), 3.8 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX), 65.2 mole % recovery of unreacted chloride, and 14.7 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane (XXII). The second fraction of the solution was carbonated after stirring for 10 minutes to give 0.0748 g of acid and 0.180 g of neutral material. These contained 10.3 mole % yield of XXI, 6.6 mole % yield of XX, 25.2 mole % recovery of chloride, and 14.7 mole % yield of XXII. The third fraction was carbonated after a total of 17 minutes of stirring to give 0.109 g of acid and 0.075 g of neutral material. These by G. C. analysis contained 22.0 mole % yield of XXI, 14.4 mole % yield of XX, 4.4 mole % recovery of unreacted chloride, and 22.4 mole % yield of XXII. At this time, the color of the solution turned from red to green. To the solution was added 10.0 ml (0.676 g-atom) of mercury in a fine stream during a period of two and a half minutes. The last fraction was carbonated after stirring for a total of 26 minutes to give 0.196 g of acid and 0.129 g of neutral material. These products contained 13.2 mole % yield of XXI, 9.7 mole % yield of XX, 3.8 mole % recovery of unreacted chloride, and 27.1 mole % yield of XXII.

In run four, 6.19 g (0.0815 g-atom) of Cs-K-Na alloy (same composition as in run one) and 1.14 g (0.00418 mole) of the chloride were allowed to react. The addition of the chloride solution took 16 seconds. After stirring for another 7 minutes, the color of the solution turned from red to green. A portion of the solution was carbonated to give 0.180 g of acid and 0.0894 g of neutral material. To the rest of the solution was added 15 ml (1.01 g-atom) of mercury. The solution was

stirred for 40 seconds. The second fraction of solution was carbonated after standing for another 6.5 minutes (totally 15.1 minutes after completion of addition of the chloride to give 0.165 g of acid and 0.0619 g of neutral material. The third fraction was carbonated after a total of 21.7 minutes after completion of addition of the chloride to give 0.178 g of acid and 0.0654 g of neutral material. The fourth fraction was carbonated at 28.7 minutes after completion of addition of the chloride to give 0.277 g of acid and 0.113 g of neutral material.

Quantitative G. C. analyses gave for the first fraction, 3.71 mole % recovery of unreacted chloride, 23.0 % mole % yield of 2-p-biphenylyl-2,3-dimethylbutane (XXII), 24.9 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXI), and 12.7 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX); the second fraction gave similarly 1.2% of unreacted chloride, 20.4% of XXII, 19.5% of XXI, and 9.9% of XX; the third fraction, 1.2% of unreacted chloride, 21.3% of XXII, 15.6% of XXI, and 8.2% of XX, the fourth fraction, 0.82% of unreacted chloride, 21.3% of XXII, 12.8% of XXI, and 5.6% of XX.

In run five, 5.31 g (0.0710 g-atom) of Cs-K-Na alloy (containing 40.5 atom % of Cs, 45.7 atom% of K, 13.8 atom % of Na) was allowed to react with 1.28 g (0.00460 mole) of the chloride in THF at -75°. After addition of the chloride was finished in 12 seconds, a portion of the solution was carbonated to give, after work up, 0.264 g of acid and 0.092 g of neutral material. These by quantitative G. C. analysis contained 1.7 mole % recovery of unreacted chloride, 22.5 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane (XXII), 15.2 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXI),

and 5.9 mole % of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX). The rest of the solution was warmed to -50 to -53° in 4 minutes by removing the dry ice bath. The second fraction of solution was carbonated to give 0.284 g of acid and 0.099 g of neutral material. These contained 13.1 mole % yield of XXI, 4.2 mole % yield of XX, 1.3 mole % recovery of unreacted chloride, and 22.3 mole % yield of XXII. The rest of the solution was carbonated after standing at -50° for 6 minutes, to give 0.405 g of acid and 0.156 g of neutral material. Quantitative G. C. analysis showed the presence of 9.9 mole % yield of XXI, 3.2 mole % yield of XX, 1.2 mole % recovery of unreacted chloride, and 22.0 mole % yield of XXII.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy in Presence of t-BuOH

The reaction was run in 250 ml of freshly distilled THF in a 500-ml Morton flask equipped with a high-speed stirrer, condensor, and addition funnel. To the flask was added 6.17 g (0.0812 g-atom) of Cs-K-Na alloy (containing 41.1 atom % of Cs, 48.4 atom % of K, 10.5 atom % of Na). The reaction mixture was stirred at room temperature for 20 minutes and then at -75° for another 20 minutes. A solution of 0.806 g (0.00296 mole) of the chloride and 0.898 g (0.0121 mole) of t-BuOH in 22 ml of THF was added during a period of 20 seconds. After stirring for another 25 seconds, the solution was syphoned onto excess freshly crushed Dry Ice. The usual work up yielded 0.741 g of neutral material which by quantitative G. C. analyses contained 10 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane (XXII) and 71 mole % recovery of chloride.

The ^{1}H NMR spectrum of the crude product indicated 82.4 mole % of unreacted chloride and 11.0 mole % yield of compound XXII.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy Followed by Addition of Trimethylsilyl Chloride

This reaction was run using 200 ml of freshly distilled THF as solvent in a 500 ml Morton flask under a nitrogen atmosphere. To the solution was added 6.35 g (0.0828 g-atom) of Cs-K-Na alloy (containing 41.9 atom % of Cs, 47.5 atom % of K, 10.6 atom % of Na). The solution was stirred at room temperature for 30 minutes and then at -75° for 20 minutes. A solution of 0.909 g (0.00333 mole) of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane in 15 ml of THF was added over a period of 9 seconds. The color of the solution turned to yellow and then to red immediately. After stirring for another 34 seconds, the color turned to green. The stirring speed was reduced. A solution of 12 ml (10 mmole) of trimethylsilyl chloride dissolved in 12 ml of THF was added in 20 seconds; then the solution was syphoned onto crushed Dry Ice. The usual work up yielded 1.00 g of neutral material. Quantitative G. C. analysis showed the presence of 1.1 mole % recovery of unreacted chloride, 25.2 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, and 34.6 mole % yield of 3-p-biphenylyl-2,3-dimethyl-2-trimethylsilylbutane. Two attempts to separate the products by liquid chromatography failed. Pure 3-p-biphenylyl-2,3-dimethyl-2-trimethylsilylbutane was finally collected by preparative gas chromatography and then sublimed at 90-110° (bath temp.) and 0.15 mm to give m.p. 50.5-52.0°; ^{1}H NMR ($CDCl_3$): δ 7.3-7-7 (9 H, m), 1.47 (6 H, s), 0.92 (6 H, s), 0.00 (9 H, s); λ_{max} (EtOH)

256 nm (ε 17400); mass spectrum m/e (rel. int.): 310 (0, M^+), 223 (3), 195 (100), 181 (6), 167 (14), 153 (4).

Anal.* Calcd. for $C_{21}H_{30}Si$: C, 81.22; H, 9.74. Found: C, 81.20, 81.17; H, 9.76, 9.76.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy Followed by Addition of Dimethyl Sulfate

The reaction was run as usual in a 500-ml Morton flask with 250 ml of THF as solvent. To the flask was added 4.52 g (0.0602 g-atom) of Cs-K-Na alloy (containing 40.5 atom % of Cs, 46.8 atom % of K, 12.7 atom % of Na). The solution was stirred at room temperature for 30 minutes and then at -75° for another 20 minutes. A solution of 0.662 g (0.00243 mole) of the chloride in 16 ml of THF was added by syringe in 2 seconds. After stirring for another 21 seconds, the color of the solution turned from red to green. A small fraction of the solution was carbonated to give, after work up, 12.7 mg of acid and 16.6 mg of neutral material. These by quantitative G. C. analysis contained 15.7 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, 12.4 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid, 25 mole % recovery of unreacted chloride and 8.9 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane. To the rest of the solution was added 40 ml (0.42 mole) of dimethyl sulfate. The solution was stirred for 5 seconds and then syphoned onto crushed Dry Ice. The usual work-up yielded 0.691 g of product which by quantitative G. C. analysis contained 11.4 mole %

*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

recovery of chloride, 26.5 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, and 29.8 mole % yield of 2-p-biphenylyl-2,3,3-trimethylbutane. The ^{1}H NMR spectrum of this crude product gave a ratio of vinyl hydrogens to aromatic hydrogens of 18 to 870 which might refer to the presence of 5% of spirocyclic product if there was any.

Attempt to separate the crude product mixture by high pressure liquid chromatography on Merck silica gel 60 failed. Pure 2-p-biphenylyl-2,3,3-trimethylbutane was finally collected by preparative G. C. and recrystallized from hexane to give crystals with m.p. 78-79°; ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9 H, m, with sharp s at 7.53), 1.39 (6 H, s), 0.87 (9 H, s); λ_{max} (EtOH) 252 nm (ε 20,500); mass spectrum m/e (rel. int.): 252 (2, M^+), 236 (2), 195 (100), 167 (13).

Anal.* Calcd. for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.24, 90.31; H, 9.61, 9.60.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy Followed by Addition of MeI

The reaction was run as usual under a nitrogen atmosphere. Into a 500-ml Morton flask was distilled 250 ml of THF and then 5.58 g (0.0743 g-atom) of Cs-K-Na alloy (containing 40.5 atom % of Cs, 46.8 atom % of K, 12.7 atom % of Na) was added. The solution was stirred at room temperature for 30 minutes and at -75° for another 30 minutes. A solution of 0.664 g (2.43 mmole) of the chloride in 16 ml of THF was added during a period of 11 seconds and the mixture stirred for another 2 seconds. The

*Analysis by Atlantic Microlab, Inc., Atlanta, Georgia.

stirring speed was reduced and 16.0 ml (0.257 mole) of methyl iodide was added by a syringe over a period of 5 seconds. All the solution was syphoned onto excess crushed Dry Ice. The usual work-up yielded 0.630 g of product. Quantitative G. C. analysis gave 25.8 mole % yield of 3-p-biphenylyl-2,3-dimethyl-1-butene, 35.5 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, and 8.4 mole % yield of 2-p-biphenylyl-2,3,3-trimethylbutane.

Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy Followed by Treatment with Lithium Bromide and Lithium t-Butoxide

The reaction was run as usual by allowing 6.58 g (0.0876 g-atom) of Cs-K-Na alloy (containing 40.5 atom % of Cs, 46.8 atom % of K, 12.7 atom % of Na) to react with 0.676 g (0.00248 mole) of the chloride in 250 ml of THF at -75°. The slurry of lithium bromide and lithium t-butoxide was made by adding 25 ml of 2.6 M n-BuLi solution in hexane to a mixture of 1.34 g (0.0180 mole) of t-BuOH and 2.08 g (0.0240 mole) of LiBr in 15 ml of THF. After the organolithium compound was formed in 22 seconds, a small fraction of the solution was carbonated; the usual work-up gave 0.0912 g of acid and 0.0511 g of neutral material. These by quantitative G. C. analyses contained 2.95 mole % recovery of unreacted chloride, 22.9 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, 16.1 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, and 7.8 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid. To the rest of the solution was added all the slurry of LiBr and t-BuOLi through a big needle syringe. After stirring for 8

seconds, all the solution was carbonated. The usual work-up gave 0.314 g of acid and 0.230 g of neutral material. These by quantitative G.C. analysis contained 2.17 mole % recovery of unreacted chloride, 23.9 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, 0.10 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, and 24.1 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid.

Attempts to React 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy Followed by Addition of Trimethyloxonium Tetrafluoroborate

In run one, 5.04 g (0.0670 g-atom) of Cs-K-Na alloy (containing 40.6 atom % of Cs, 46.7 atom % of K, 12.7 atom % of Na) was allowed to react with 0.727 g (0.00261 mole) of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane in THF at -75°. The organocesium compound was made in 40 seconds, then, 2.67 g (0.0181 mole) of trimethyloxonium tetrafluoroborate was added as a crystalline solid. After stirring for 15 seconds, the solution was carbonated to give, 0.356 g of neutral material and 0.383 g of acid. Quantitative G. C. analyses of the acid as methyl ester and the neutral material gave 6.1 mole % recovery of unreacted chloride, 29.1 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane, 18.4 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, and 6.6 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid; no methylation product could be detected.

In run two, 4.38 g (0.0586 g-atom) of Cs-K-Na alloy (containing 40.0 atom % of Cs, 48.8 atom % of K, 11.2 atom % of Na) was placed in a 500-ml Morton flask under a nitrogen atmosphere. Dimethyl ether, 250

ml, was introduced directly from a cylinder and condensed onto the alloy. The solution was stirred at the boiling point (-25°) of dimethyl ether for one hour, and then at -75° for 30 minutes. A solution of 0.873 g (0.00320 mole) of the chloride in 25 ml of dimethyl ether and 5 ml of diethyl ether was added rapidly. Solution was stirred at -75° for 14 minutes with no sign of reaction and then at -25° for another 25 minutes with still no sign of reaction. To this solution was added a slurry of 1.78 g (0.0121 mole) of trimethyloxonium tetrafluoroborate in 25 ml of dimethyl ether via a big syringe. After stirring for another 10 minutes, the solution was syphoned onto excess crushed Dry Ice. The usual work up yielded 0.844 g of neutral material which by G. C. and NMR analysis was exclusively unreacted starting chloride.

In run three, 0.885 g (0.00324 mole) of the chloride was allowed to react with 5.39 g (0.0721 g-atom) of Cs-K-Na alloy (containing 40.0 atom % of Cs, 48.8 atom % of K, 11.2 atom % of Na) in THF at -75° for 6 minutes; then 15.0 ml (1.014 g-atom) of Hg was added through a constant addition funnel during a period of 5 minutes. After two thirds of the mercury was added, 4.17 g (0.0282 mole) of trimethyloxonium tetrafluoroborate contained in a bulb attached to a neck of the reaction flask by a standard tape joint was added by rotation of the bulb about the joint until the contents fell into the Morton flask. The solution was stirred vigorously for 18 minutes, and then syphoned onto crushed Dry Ice. The usual work up yielded 0.592 g of acid and 0.611 g of neutral material. Quantitative G. C. analyses of the acid as methyl ester and the neutral material gave 4.4 mole % yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, 2.5 mole % yield of

3-p-biphenylyl-2,2,3-trimethylbutanoic acid, 7.2 mole % recovery of unreacted chloride, and 28 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane; no methylation product was detected.

Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 with Lithium

The mixture of 67% of 3-p-biphenylyl-2-chloro-3-methyl-2-(methyl-d_3) butane-1,1,1-d_3 and 33% of 3-p-biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 was used. The reaction was run as usual using 500-ml Morton flask containing 200 ml of freshly distilled THF as solvent. Lithium metal, 0.812 g (0.117 g-atom), was cut into small pieces and added to the flask. To the solution were added 0.6 ml of methyl iodide and 10 drops of the starting chloride solution (totally 0.607 g, 0.00218 mole in 20 ml of THF) at -15°. After stirring rapidly for 40 minutes at this temperature, a pink color developed which turned to light brown in 3 minutes. The solution was cooled to -75°. The rest of the chloride solution was added slowly. After stirring for another 60 minutes, the solution turned dark brown. Carbonation and the usual work-up gave 0.198 g of acid and 0.457 g of neutral material. These by quantitative G. C. analysis contained 8.2 mole % recovery of unreacted chloride, 42.8 mole % yield of 2-p-biphenylyl-2,3-dimethylbutane(-d_6), and 19.9 mole % yield of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid(-d_6). The crude neutral material had ^{1}H NMR ($CDCl_3$): δ 7.3-7.7 (9.00 H, m), 1.57 (0.34 H, two overlapping s, from the chloride), 1.25 (2.31 H, s, from compound XXXI), 0.80 (3.11 H, d, J = 7 Hz, from compound XXXII). This spectrum indicated that the neutral material contained 2-p-biphenylyl-

-2-methyl-3-(methyl-$\underline{d}_3$)butane-$\underline{4},\underline{4},\underline{4}$-$\underline{d}_3$ (XXXI) and 2-$\underline{p}$-biphenylyl-3-methyl-2-(methyl-$\underline{d}_3$)butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ (XXXII) with the ratio of 1.00/1.35. After one recrystallization from hexane, the acidic product (m.p. 207.0-208.5°) had ^{1}H NMR: δ 10.4 (1.0 H, s), 7.3-7.7 (9.0 H, m), 1.53 (2.3 H, s), 1.14 (3.7 H, s), indicating that it contained 3-$\underline{p}$-biphenylyl-2,2-(dimethyl-$\underline{d}_6$)-3-methylbutanoic acid (XXVII) and 3-$\underline{p}$-biphenylyl-2,2-dimethyl-3-(methyl-$\underline{d}_3$(butanoic acid-$\underline{4},\underline{4},\underline{4}$-$\underline{d}_3$ (XXVIII) in the ratio of 38 : 62.

Reaction of 3-$\underline{p}$-biphenylyl-2-chloro-3-methyl-2-(methyl-$\underline{d}_3$) butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ with Lithium in Presence of $\underline{t}$-Butanol

The previous reaction was repeated by reacting 1.78 g (0.257 g-atom) of lithium with 0.776 g (0.0275 mole) of the same labeled chloride, but in presence of 2.01 g (0.0271 mole) of $\underline{t}$-BuOH. The reaction was initiated at -15° by adding 5 drops of the chloride solution (totally in 16 ml of THF), 0.2 ml of methyl iodide and 2.0 ml of 2.5 N $\underline{n}$-BuLi to a 500 ml Morton flask containing 250 ml of THF and the lithium pieces. After stirring rapidly for 60 minutes, the solution cooled to -75°, and $\underline{t}$-BuOH mixed with the chloride was added slowly. After stirring for another 2 hours, the solution was syphoned onto crushed Dry Ice. The usual work-up yielded 0.817 g of neutram material. Quantitative G. C. analysis showed that it contained 37.8 mole % recovery of unreacted chloride and 41.1 mole % yield of 2-$\underline{p}$-biphenylyl-2,3-dimethylbutane(-$\underline{d}_6$). The crude product had a ^{1}H NMR spectrum δ 7.3-7.7 (9.0 H, m), 1.56 and 1.58 (2.8 H, overlapping s, methyl hydrogens of chloride), 1.24 (1.8 H, s, methyl hydrogens of XXXI), 0.80 (1.2 H, d, J = 7 Hz, methyl hydrogens of XXXII). This proved that the ratio of

2-p-biphenylyl-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 (XXXI) to 2-p-biphenylyl-2-(methyl-d_3)-3-methylbutane-1,1,1-d_3 (XXXII) in the product was 1.5 : 1.0.

Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)-butane-1,1,1-d_3 with Cs-K-Na Alloy

The reaction was run as usual in a dry box with 250 ml of freshly distilled THF as solvent in a 500-ml Morton flask equipped with high-speed stirrer, addition funnel, and condensor. To the flask was added 11.1 g (0.148 g-atom) of Cs-K-Na alloy (containing 40.5 atom % of Cs, 45.7 atom % of K, 13.8 atom % of Na). The solution was stirred rapidly at room temperature for 30 minutes, then, at -75° for another 30 minutes. To this solution was added 1.78 g (0.00639 mole) of the starting chloride mixture (containing 67% of 3-p-biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 and 33% of 3-p-biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3) in 20 ml of THF over a period of 13 seconds. The color of the solution changed from blue to yellow, then red immediately. After another 12 seconds of stirring, solution turned to green. Stirring was stopped. Half of the solution was carbonated. The rest of the solution was kept at -75° for 10 minutes and then carbonated. The usual work up yielded, for the first fraction, 0.492 g of acid and 0.233 g of neutral material, and the second fraction, 0.860 g of acid and 0.318 g of neutral material. The acidic product in the two fractions were separated by liquid chromatography through a glass column (120 cm long with 3.6 cm diameter) packed with 230 g of Merck-Darmstadt silica gel (70-325 mesh, with packing height of 50 cm) with hexane-ether (60/40)

as eluant. Proton NMR spectra of the acids collected gave the ratio of isomers with different positions of the deuterium label as listed in Table 2. From the NMR spectra of the purified acids and quantitative G. C. analyses of the crude products, the first fraction contained 1.1 mole % of unreacted chloride, 2.3 mole % of 3-p-biphenylyl-2,2-(dimethyl-d_6)-3-methylbutanoic acid (XXVII), 3.7 mole % of 3-p-biphenylyl-2,2-dimethyl-3-(methyl-d_3)butanoic acid-4,4,4-d_3 (XXVIII), 10 mole % of 1,1-dimethyl-2,2-(dimethyl-d_6)-6-phenyl-spiro[2.5]octa-4,7-diene-6-carboxylic acid (XXIX), 10 mole % of 1,1-(dimethyl-d_6)-2,2-dimethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXX), 9.4 mole % of 2-p-biphenylyl-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 (XXXI), and 11.1 mole % of 2-p-biphenylyl-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 (XXXII). The second fraction gave 1.5 mole % of XXVII, 2.5 mole % of XXVIII, 7.8 mole % of XXIX, 7.8 mole % of XXX, 9.1 mole % of XXXII, 7.8 mole % of XXXI, and 0.6 mole % of unreacted chloride.

Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)-butane-1,1,1-d_3 with Cs-K-Na Alloy in Presence of t-BuOH

The reaction was run by reacting 6.52 g (0.0872 g-atom) of Cs-K-Na alloy (containing 40.5 atom % of Cs, 45.7 atom % of K, 13.8 atom % of Na) with 0.379 g (0.00136 mole) of the chloride mixture (same composition as in previous reaction) in presence of 0.370 g (0.00499 mole) of t-BuOH in 250 ml of THF at -75°. The chloride and t-BuOH in 18 ml of THF were added to the reaction solution over a period of 12 seconds. After stirring for another 18 seconds, the solution was syphoned onto

Table 2. Some Spectroscopic Data of the Products from Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)-butane-1,1,1-d_3 with Cs-K-Na Alloy in THF at -75°

Fractions	Products	Chemical Shift of Critical Peaks (δ)	# of H	Mass Spec. m/e (rel. int.)	Product** Identified
1.	Spiro Acid	1.19 (s)*	6.00		XXIX and
		1.14 (s)	6.00		XXX
	Open Form Acid	1.53 (s)	2.31	195 (63)	XXVII
		1.14 (s)	3.69	201 (100)	XVIII
	Protonated Product	1.24 (s)	2.74	195 (82)	XXXI
		0.80 (d)	3.25	201 (100)	XXXII
2.	Spiro Acid	1.19 (s)	6.00		XXIX and
		1.14 (s)	6.00		XXX
	Open Form Acid	1.53 (s)	2.32		XXVII
		1.14 (s)	3.67		XXVIII
	Protonated Product	1.24 (s)	2.75		XXXI
		0.80 (d)	3.25		XXXII

*Multiplicity

** XXIX : 1,1-Dimethyl-2,2-(dimethyl-d_6)-6-phenylspiro[2.5]-octa-4,7-diene-6-carboxylic Acid

XXX : 1,1-(Dimethyl-d_6)-2,2-dimethyl-6-phenylspiro[2.5]-octa-4,7-diene-6-carboxylic Acid

XXVII : 3-p-Biphenylyl-2,2-(dimethyl-d_6)-3-methylbutanoic Acid

XXVIII : 3-p-Biphenylyl-2,2-dimethyl-3-(methyl-d_3)butanoic Acid-4,4,4-d_3

XXXI : 2-p-Biphenylyl-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3

XXXII : 2-p-Biphenylyl-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3.

crushed Dry Ice. The usual-up of the product yielded 0.396 g of neutral material. Quantitative G. C. analysis gave 70.3 mole % of unreacted chloride and 19.9 mole % of protonated product. The crude product was separated by liquid chromatography through a glass column (length 117 cm, diameter 26 mm) packed with 100 g of Merck-Darmstadt silica gel (70-325 mesh) using hexane as eluant, to give 34 mg of pure protonated product whose NMR spectrum, δ 1.24 (3.3 H, s), 0.80 (2.7 H, d), showed that it contained 2-p-biphenylyl-2-methyl-3-(methyl-$\underline{d}_3$)-butane-4,4,4-$\underline{d}_3$ (XXXI) and 2-p-biphenylyl-3-methyl-2-(methyl-$\underline{d}_3$)butane-1,1,1-$\underline{d}_3$ (XXXII) in the ratio of 1.2 : 1.0.

Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-$\underline{d}_3$)-butane-1,1,1-$\underline{d}_3$ with Cs-K-Na Alloy in Presence of Methanol

The previous reaction was repeated by reacting 6.44 g (0.0858 g-atom) of Cs-K-Na alloy (containing in atom percent: 40.5% of Cs, 46.8% of K, 12.7% of Na) with 0.630 g (0.00226 mole) of the chloride mixture (same composition as in previous reaction), but in presence of 1.0 ml (0.0247 mole) of methanol, in 250 ml of THF at -75° for 35 seconds. The solution was quenched by syphoning onto crushed Dry Ice. The usual work-up yielded 0.518 g of neutral material. Quantitative G. C. analyses gave 14.2 mole % of unreacted chloride, 42.9 mole % of 2-(4-cyclohexylphenyl)-2,3-dimethyl-butane(-$\underline{d}_6$) (identified by comparisons of the G. C. retention time, NMR and mass spectrum with an authentic sample synthesized), and 11.6% of 2-p-biphenylyl-2,3-dimethylbutane(-$\underline{d}_6$). The crude product was separated by HPLC through a glass column (100 cm long and 2.5 cm in diameter) filled with Merck silica gel 60 using hexane as eluant. The

first component (50 mg) collected was analyzed by its NMR spectrum, δ 7.3-7.7 (4.00 H, m), 1.24 (3.56 H, s), 0.75 (2.42 H, d, J = 6 Hz), to contain 2-(4-cyclohexylphenyl)-2-methyl-3-(methyl-$\underline{d}_3$)butane-$\underline{4},\underline{4},\underline{4}$-$\underline{d}_3$ and 2-(4-cyclohexylphenyl)-3-methyl-2-(methyl-d_3)butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ in the ratio of 1.47/1.00. The mass spectrum of this mixture gave this ratio as 1.50/1.00 based upon the peaks at m/e (rel. int.): 201 (49.5) and 207 (33.0). The second component (36 mg) collected was analyzed by its NMR spectrum, δ 7.3-7.7 (9.0 H, m), 1.24 (3.5 H, s), 0.80 (2.5 H, d), to contain 2-$\underline{p}$-biphenylyl-2-methyl-3-(methyl-$\underline{d}_3$)butane-$\underline{4},\underline{4},\underline{4}$-$\underline{d}_3$ and 2-$\underline{p}$-biphenylyl-3-methyl-2-(methyl-$\underline{d}_3$)butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ in the ratio of 1.40/1.00.

Reaction of 3-$\underline{p}$-Biphenylyl-2-chloro-3-methyl-2-(methyl-$\underline{d}_3$)-butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ with Cs-K-Na Alloy Followed by Addition of Water

Into a 500-ml Morton flask containing 200 ml of freshly distilled THF was put 7.52 g (0.0980 g-atom) of Cs-K-Na alloy (containing by atom percent 41.9% of Cs, 47.5% of K, 10.6% of Na). The solution was stirred at room temperature for 25 minutes and then at -75° for another 25 minutes. To this solution was added a solution of 0.640 g (0.00229 mole) of the chloride mixture (containing 67% of 3-$\underline{p}$-biphenylyl-2-chloro-3-methyl-2-(methyl-$\underline{d}_3$)butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ and 33% of 3-$\underline{p}$-biphenylyl-2-chloro 2-methyl-3-(methyl-$\underline{d}_3$)butane-$\underline{4},\underline{4},\underline{4}$-$\underline{d}_3$) in 17 ml of THF during a period of 12 seconds. The color of the solution changed from blue to yellow,

red, then green in another 30 seconds of stirring. The solution was syphoned onto an ice slurry. The usual work up yielded 0.608 g of crude product. Quantitative G. C. analyses gave 3.4 mole % of unreacted chloride and 40.7 mole % of 2-p-biphenylyl-2,3-dimethylbutane(-d_6). The crude product was separated by HPLC through a glass column (100 cm long, 2.5 cm in diameter) filled with EM grade silica gel 60 (mesh 30-70 ASTM) using cyclohexane as eluant. Pure 2-p-biphenylyl-2,3-dimethylbutane (172 mg) was analyzed by NMR spectrum, δ 7.3-7.7 (9.0 H, m), 1.24 (2.3 H, s), 0.80 (3.7 H, d) to contained 2-p-biphenylyl-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 and 2-p-biphenylyl-2-methyl-3-(methyl-d_3)-butane-4,4,4-d_3 with the ratio of 1.6/1.0.

Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)-butane-1,1,1-d_3 with Cs-K-Na Alloy Followed by Addition of Trimethylsilyl Chloride

The chloride mixture used contained 67% of 3-p-biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 and 33% of 3-p-biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3.

The reaction was run as usual in a dry box in a 500-ml Morton flask with 250 ml of freshly distilled THF as solvent. To the flask was added 5.80 g (0.0774 mole) of Cs-K-Na alloy (containing by atom percent 41.0% of Cs, 45.1% of K, and 13.9% of Na). The solution was stirred at room temperature for 30 minutes and then at -75° for another 20 minutes. To this cold solution was added 0.762 g (0.00273 mole) of the chloride mixture in 16 ml of THF during a period of 15 seconds. The color of the

solution soon changed from blue to yellow, red, then green in another 17 seconds of stirring. A solution of 18 ml (16 mmole of trimethylsilyl chloride mixed with 18 ml of THF was added during a period of 12 seconds. The solution was syphoned onto excess crushed Dry Ice. The usual work-up yielded 1.16 g of neutral material. Quantitative G. C. analyses gave 3.5 mole % of unreacted chloride, 22.7 mole % of 2-p-biphenylyl-2,3-dimethylbutane-($-d_6$), and 19.4 mole % of 3-p-biphenylyl-2,3-dimethyl-2-trimethylsilylbutane($-d_6$). These products were collected by preparative G. C. and analyzed by an NMR technique to contain, in the protonation product (with δ 7.3-7.7 (9.0 H, m), 1.24 (2.3 H, s), 0.80 (3.7 H, d)), 2-p-biphenylyl-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 and 2-p-biphenylyl-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 in a ratio 1.0/1.6, and in the silylation product with δ 7.3-7.7 (9.0 H, m), 1.47 (2.2 H, s), 0.92 (3.8 H, s)) 3-p-biphenylyl-2-(methyl-d_3)-3-methyl-2-trimethylsilylbutane-1,1,1-d_3 and 3-p-biphenylyl-2-methyl-3-(methyl-d_3)-2-trimethylsilylbutane-4,4,4-d_3 in a ratio 1.0/1.7.

Reaction of the Mixture of 3-p-Biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 and 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 with Cs-K-Na Alloy

The chloride mixture containing 54.5% of 3-p-biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 and 45.5% of 3-p-biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 was used in this reaction. The reaction was run as usual in dry box using a 500 ml Morton flask equipped with a high-speed stirrer, addition funnel, and condensor with

250 ml of freshly distilled THF as solvent. To the flask was added 5.88 g (0.0786 g-atom) of Cs-K-Na alloy (containing by atom percent 40.0% of Cs, 48.8% of K, and 11.2% of Na). The solution was stirred at room temperature for 30 minutes and then at -75° for another 20 minutes. A solution of 0.917 g (0.00329 mole) of the starting chloride mixture in 20 ml of THF was added over a period of 8 seconds. The color of the solution changed from blue to yellow, then red. The solution was stirred for another 46 seconds until the color turned to green, and then the solution was carbonated. The usual work up yielded 0.631 g of acid and 0.308 g of neutral material. Quantitative G. C. analyses of the acid as methyl ester and the neutral material gave 27.6 mole % of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid(-$\underline{d}_6$), 8.4 mole % of 3-$\underline{p}$-biphenylyl-2,2,3-trimethylbutanoic acid(-$\underline{d}_6$), 1.1 mole % of unreacted chloride and 32.2 mole % of 2-$\underline{p}$-biphenylyl-2,3-dimethylbutane(-$\underline{d}_6$). The non-spiro acidic product was collected on preparative G. C. as methyl ester and analyzed by an NMR technique (δ 7.3-7.7 (9.0 H, m), 1.53 (2.3 H, s), 1.14 (3.7 H, s)) to give 3-$\underline{p}$-biphenylyl-2,2-(dimethyl-$\underline{d}_6$)-3-methylbutanoic acid and 3-$\underline{p}$-biphenylyl-2,2-dimethyl-3-(methyl-$\underline{d}_3$)-butanoic acid-$\underline{4},\underline{4},\underline{4}$-$\underline{d}_3$ in a ratio of 1.0/1.6. The protonation product was collected on preparative G. C. and analyzed by a NMR technique (δ 7.3-7.7 (9.0 H, m), 1.24 (2.6 H, s), 0.80 (3.4 H, d)) to give 2-$\underline{p}$-biphenylyl-2-methyl-3-(methyl-$\underline{d}_3$)-butane-$\underline{4},\underline{4},4$-$\underline{d}_3$ and 2-$\underline{p}$-biphenylyl-3-methyl-2-(methyl-$\underline{d}_3$)butane-$\underline{1},\underline{1},\underline{1}$-$\underline{d}_3$ in a ratio of 1.0/1.3.

CHAPTER V

DISCUSSION

Syntheses

3-p-Biphenylyl-1-chloropropane

This chloride was prepared in overall yield of about 31% from biphenyl according to the synthetic route shown in Figure 1. The first intermediate 1-p-biphenylyl-1-oxopropane was prepared in 84% yield from biphenyl with propionyl chloride in presence of aluminum chloride. A 71.5% yield of the second intermediate 3-p-biphenylylpropanoic acid was obtained via the Willgerodt reaction. Reduction of the acid with $LiAlH_4$ was carried out in THF to form the corresponding carbinol in a yield of 77%. The title chloride was first synthesized by reacting the

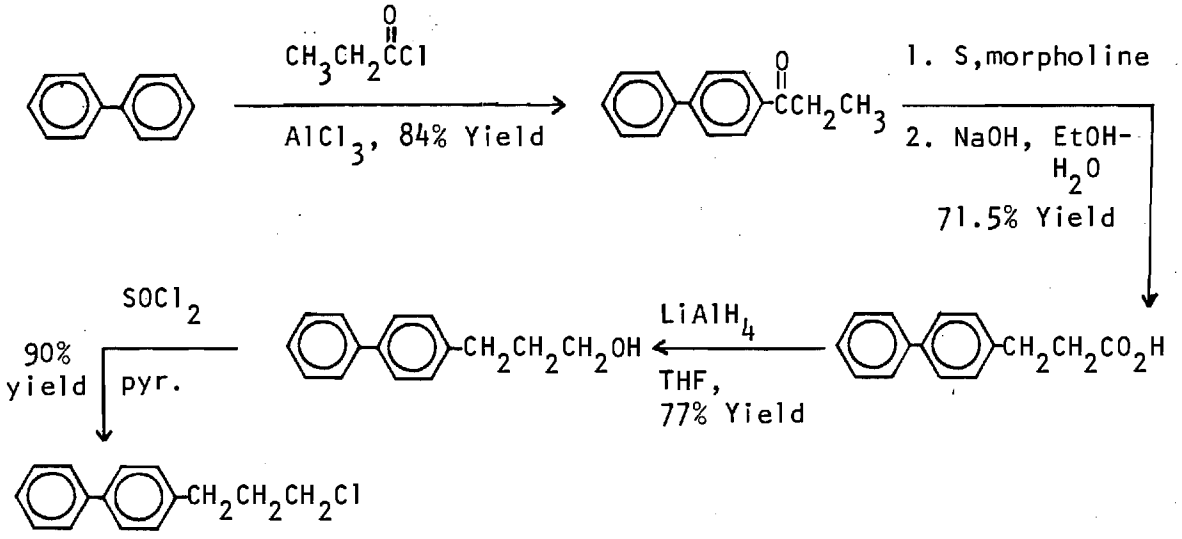


Figure 1. Synthetic Route to 3-p-Biphenylyl-1-chloro-Propane.

carbinol with excess thionyl chloride in presence of 9-fold of pyridine to give a 34% yield. It was finally formed in 90% yield by reacting the carbinol with excess thionyl chloride in presence of one-fold pyridine.

1-p-Biphenylyl-2-chloro-2-methylpropane

This chloride was synthesized in an overall yield of about 50% from biphenylylacetonitrile according to the synthetic route in Figure 2. Biphenylylacetonitrile was hydrolyzed by hydrochloric acid, and the corresponding acid was allowed to react with excess diazomethane to form a methyl ester in 58% overall yield. A Grignard reaction of this methyl ester gave a 93% yield of 3-p-biphenylyl-2-methyl-2-propanol. The transformation of this carbinol into the corresponding chloride gave 10 to 15% of a biproduct suggested by NMR spectrum to be 1-p-biphenylyl-2-methyl-1-propene. Several recrystallizations and sublimation of the product gave a mixture containing 95% of the desired chloride, and 5%

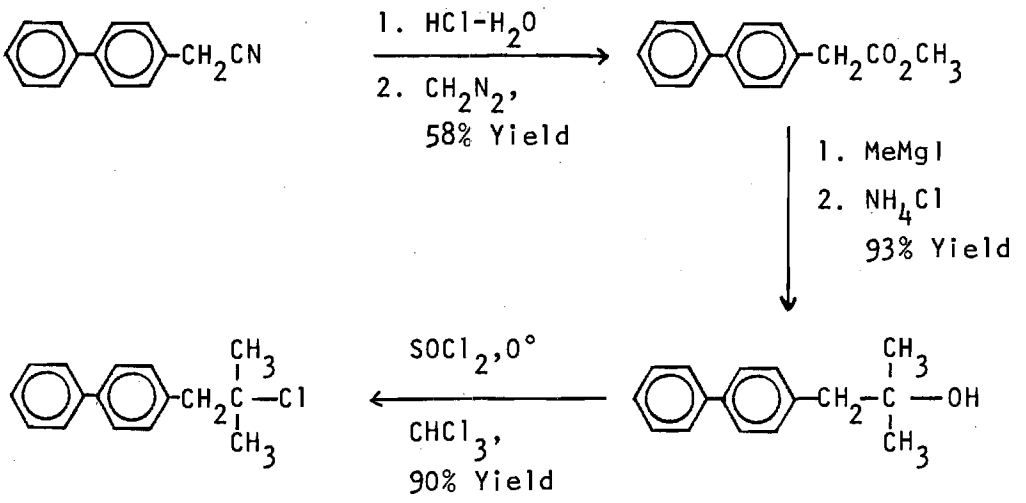


Figure 2. Synthetic Route to 1-p-Biphenylyl-2-chloro-2-methylpropane.

of the undesired olefin. This mixture was used for all the reactions of 1-p-biphenylyl-2-chloro-2-methylpropane with alkali metals.

3-p-Biphenylyl-2-chloro-2,3-dimethylbutane

This chloride was prepared in an overall yield of 50% from acetylbiphenylyl according to the synthetic route shown in Figure 3. The first intermediate 2-p-biphenylyl-2-propanol was formed by reaction of methyl Grignard reagent with the ketone in a yield of 90%. This alcohol was also synthesized by reacting p-biphenylylmagnesium bromide with acetone to give an average crude yield of 80% based on p-biphenylylbromide. A 96% yield of the second intermediate 2-p-biphenylyl-2-methoxypropane was obtained by reacting the corresponding carbinol with n-BuLi followed by addition of methyl iodide. Another proposed synthetic route to this ether by reacting p-bromobiphenyl with lithium

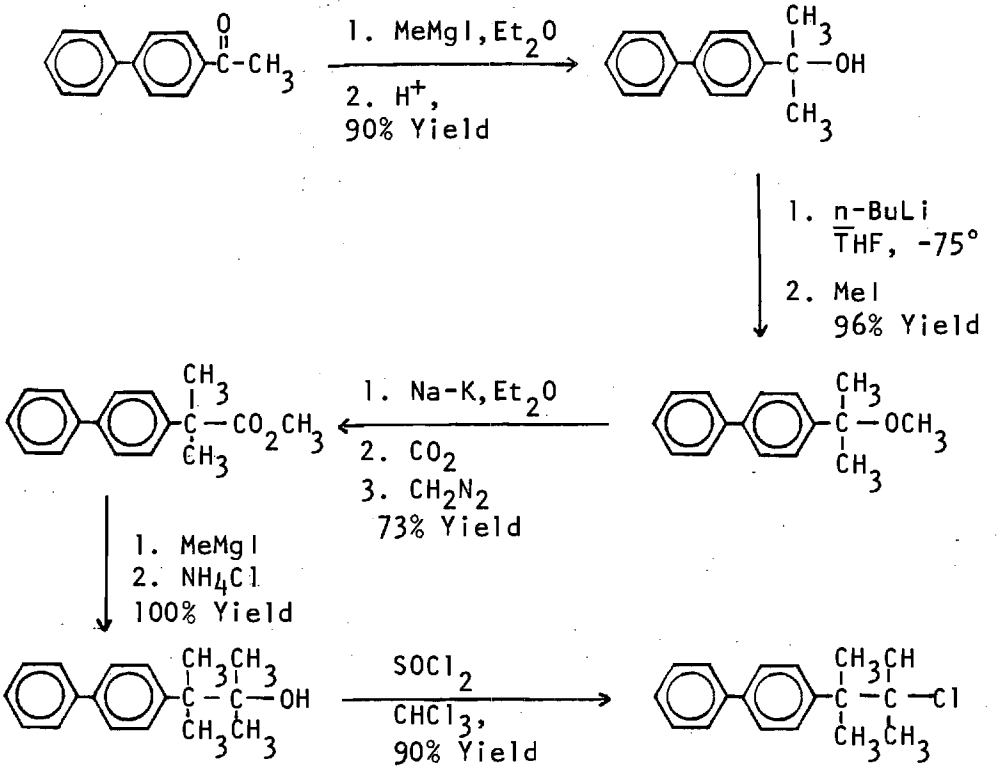


Figure 3. Synthetic Route to 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane.

metal followed by addition of acetone and then methyl iodide failed; biphenyl was obtained as the chief product. Distillation of the crude ether at 150° and 0.15 mm pressure gave the decomposition product 2-*p*-biphenylyl-1-propene. An attempt to transform this olefin back into the desired ether, through the procedure of Brown and Rei[24] by allowing it to react with mercuric acetate and methanol, gave only 65% transformation into the ether. The synthesized crude ether was used for next step without further purification. The ether was cleaved by Na-K alloy and the product carbonated to give a 73% yield of 2-*p*-biphenylyl-2-methylpropanoic acid. The methyl ester of this acid was treated with methyl Grignard reagent to give a quantitative yield of 3-*p*-biphenylyl-2,3-dimethyl-2-propanol. Attempts to synthesize this carbinol by reacting 2-*p*-biphenylyl-2-methoxypropane with either potassium in ammonia (or ether) or lithium in ether and reaction of the resulting product with acetone, failed; only *i*-propylbiphenyl was isolated. The title chloride was formed in 90% yield by reacting the carbinol with excess thionyl chloride.

3-*p*-Biphenylyl-2-chloro-3-methyl-2-(methyl-$\underline{d}_3$)butane-*1,1,1*-$\underline{d}_3$

This chloride was synthesized in an overall yield of 65 % from methyl *2*-biphenylyl-2-methylpropanoate according to the synthetic route shown in Figure 4. 3-*p*-Biphenylyl-3-methyl-2-(methyl-$\underline{d}_3$)-2-butanol-*1,1,1*-$\underline{d}_3$ was formed in 75% yield by reacting the methyl ester with perdeuteriomethyl Grignard reagent. Basic hydrolysis followed by acid-

[24] H. C. Brown and M. H. Rei, *J. Amer. Chem. Soc.*, *91*, 5646 (1969).

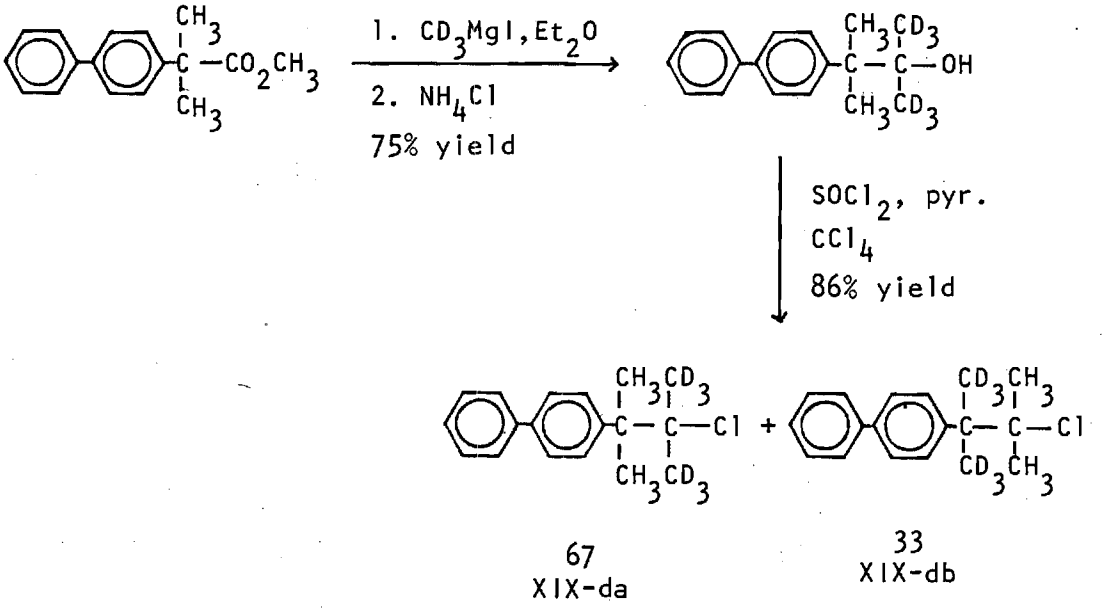
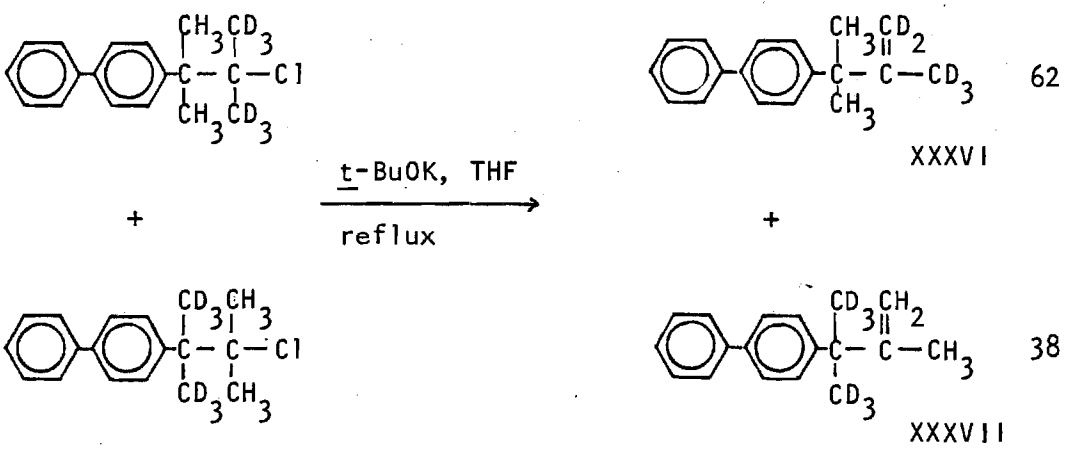


Figure 4. Synthetic Route to 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3.

base-ether extraction removed the unreacted methyl ester. The chloride was formed by reacting the labeled carbinol with thionyl chloride under different conditions as listed in Table 1. The rearranged chloride with labeling on the methyl groups nearer to the biphenyl ring was always formed as a byproduct. The best result a mixture of 67% of 3-p-biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 (XIX-da) and 33% of 3-p-biphenylyl-2-chloro-2-methyl-3-(methyl-d_3)butane-4,4,4-d_3 (XIX-db) (composition determined by its ^{1}H NMR spectrum) was obtained when one-fold of pyriding and excess of thionyl chloride in CCl_4 were used. This crude product was sublimed and recrystallized from hexane to give a pure product. The isotopic composition was confirmed by mass spectral analysis and dehydrochlorination reaction of the product. The mass spectrum of the mixture gave m/e (rel. int.) 195 (100, $C_{15}H_{15}^+$) and 201 (48, $C_{15}H_9D_6^+$).



These evidently are benzyl cleavage products of XIX-da and XIX-db respectively, and give the ratio of this two isomers to be 100:48 (or 67:33). Dehydrochlorination of this mixture with potassium t-butoxide in THF at reflux for 17 hours gave 85% yield of a mixture of 3-p-biphenylyl-2,3-dimethyl-2-(methyl-d_3)-1-butene-1,1-d_2 (XXXVI) and 3-p-biphenylyl-2-methyl-3-(methyl-d_3)-1-butene-4,4,4-d_3 (XXXVII) in the ratio of 62/38, as shown by the ^{1}H NMR spectrum: δ 4.94 (0.76 H, d), 1.56 (1.13 H, s), 1.41 (3.73 H, s). Since the dehydrochlorination reaction is likely subject to an isotope effect, the most precise analysis is thought to be that by direct NMR (or mass spectrum).

Reactions of 3-p-Biphenylyl-1-chloropropane with Alkali Metals

Reaction of 3-p-biphenylyl-1-chloropropane with Cs-K-Na alloy in THF at -75° for 33 seconds gave a dark red solution which upon carbonation yielded 35.8% of 7-phenyl-spiro[3.5]nona-5,8-diene-7-carboxylic acid (III), 6.0% of 4-p-biphenylylbutanoic acid (IV), 2.6% of 2-p-biphenylylbutanoic acid (V), 13.8% of p-biphenylylacetic acid (VI), and 23% of

n-propylbiphenyl (II) as listed in Table 3. These products are accounted for by the pathways shown in Figure 5. In agreement with this, the yield of acid III decreases with time; the intermediate spiro anion has a half life of 13 minutes and disappears on standing or raising the temperature of the reaction mixture. Since acid III has been isolated in a high yield, and the spiro anion is a major product of the initial reaction. The isolation of this derivative of the fugative spiro anion provides direct evidence for spirocyclization as a key step in aryl migration. The yield of II and V increased with time but the yield of VI decreased with time. The anion precursor of VI is likely formed by the cleavage of p-biphenylylpropyl radical to give p-biphenylylmethyl radical which is further reduced by Cs-K-Na alloy

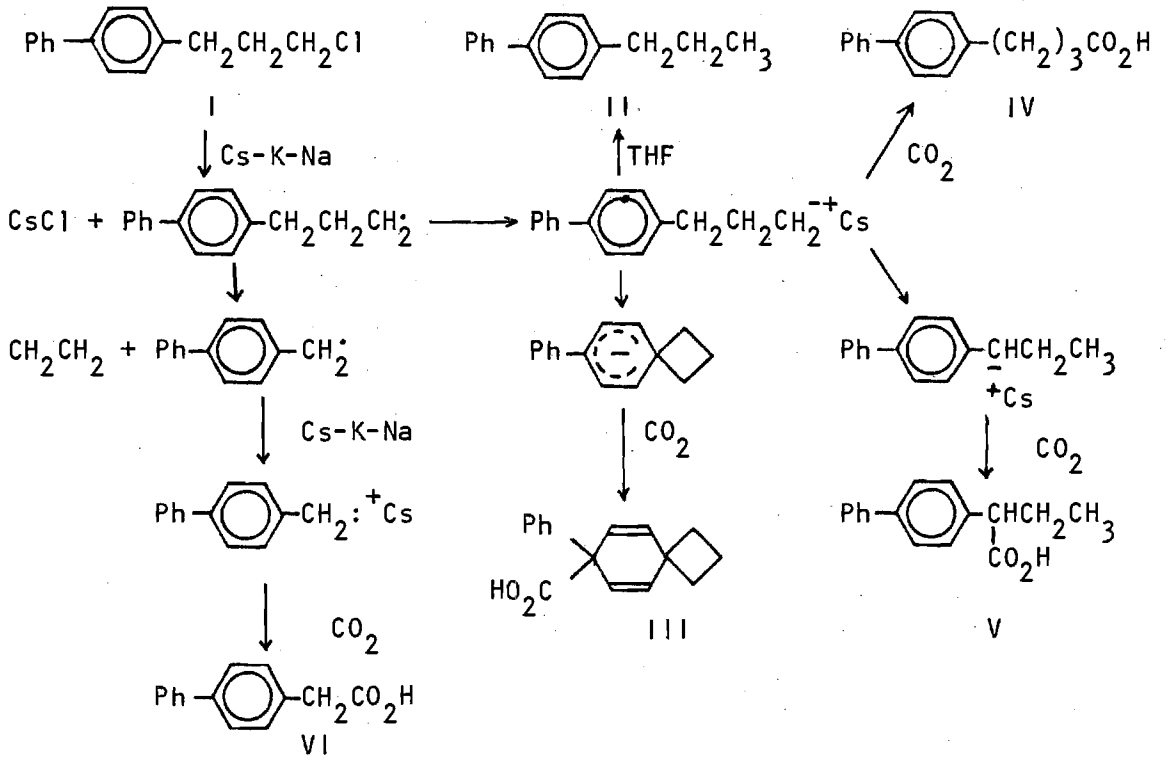
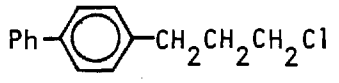
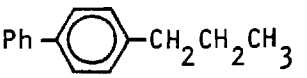


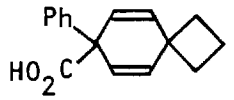
Figure 5. Reaction of 3-p-Biphenylyl-1-chloropropane with Cs-K-Na Alloy.

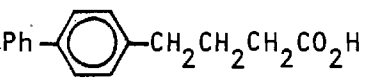
Table 3. Reaction of 3-p-Biphenylyl-1-chloropropane with Cs-K-Na Alloy

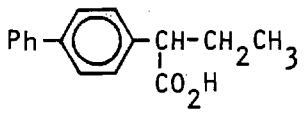
Run	Solvent	Temp.	Time (sec)	Mole % Yield Based on Chloride* I	II	III	IV	V	VI
1.	THF	-75°	540	0	19.4	0.42	2.0	6.5	5.8
2.	THF	-75°	360	1.2	24.2	12.4	1.5	3.9	8.2
		-35°	960	0.3	28.0	0	0.1	11.1	7.3
3.	THF	-75°	33	3.0	23	36	6.0	2.6	14
4.	THF	-75°	38	4.0	16.0	18	5.0	2.0	6.8
			66	3.0	14.6	17.9	4.7	2.2	6.8
			120	2.6	16.4	16.2	4.7	3.0	6.6
			180	2.2	18.0	12.7	4.2	4.2	6.4
5	THF	-75°	35	52.1	11.4	19.3	1.9	2.3	8.7
			300	3.6	23.8	12.1	0.5	3.1	5.2
			600	2.5	24.0	9.4	0.6	4.1	4.1
			900	2.0	27.4	7.1	0.1	4.5	3.5
6.	THF (+ 18-crown-6)	-75°	30	0	20.0	9.1	0	9.3	4.6
7.	THF (+ 18-crown-6)	-75°	25	0	19	12.3	0.3	10.4	3.0
8.	Et_2O	35°	1200	82.6	11	0	0	0	0.03
			1500	72.6	12	0	0.01	0.01	0.02
9.**	2-methyl-THF	-75°	63	4.1	26.2	19.5	0	0	1.3

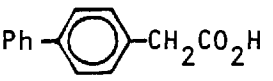
* I. 

II. 

III. 

IV. 

V. 

VI. 

**2-Methylfuran-5-carboxylic acid was isolated as biproduct in 0.1% yield based on 2-methyltetrahydrofuran.

to p-biphenylylmethylcesium. Evidently 3-p-biphenylylpropyl radical fragments more readily than 3-p-biphenylylpropylcesium.

The same reaction proceeded at a negligible rate in diethyl ether, evidently because the products of the reaction were insoluble in diethyl ether and coated the surface of the molten metal.

When 2-methyltetrahydrofuran was used as solvent for the reaction of 3-p-biphenylyl-1-chloropropane, cesium slightly dissolved at low temperature as was evident from the light blue color of the solution compared to the deep blue color of the solution (solvated elections) in THF. 2-Methylfuran, which is a stronger acid than THF evidently was present in small amounts in the sample of 2-methyl-tetrahydrofuran used as solvent as revealed by isolation of 2-methyl-furan-5-carboxylic acid. 2-Methylfuran reacted with the more reactive 3-p-biphenylylpropylcesium but not with the less reactive spiro anion; acid III was found as the only major acidic product derived from the chloropropane.

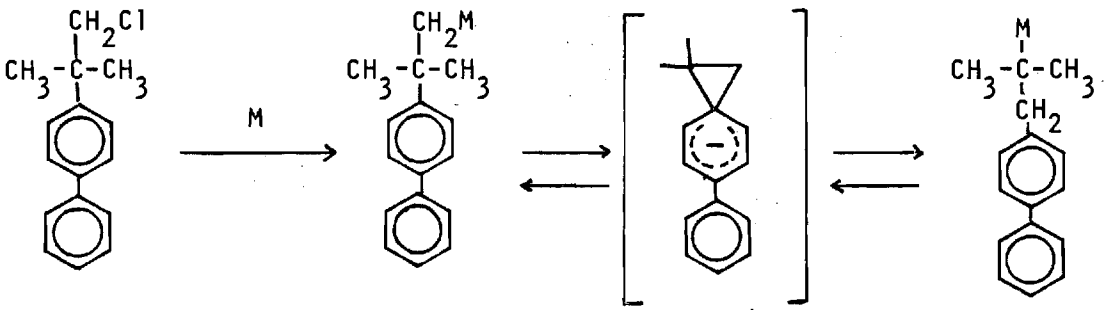
In contrast reaction of 3-p-biphenylyl-1-chloropropane with lithium metal in THF at -75° gave 3-p-biphenylylpropyllithium as the only organolithium product. This product did not cyclize even at -20°. Treatment of 3-p-biphenylylpropyllithium in THF with CsO-t-Bu (or KO-t-Bu) at -75° gave 3-p-biphenylylpropylcesium (or -potassium) evidently as a solvent-separated ion pair which underwent 1,3-proton shift to form the more stable 1-p-biphenylylpropylcesium (or -potassium). Reaction of 3-p-biphenylylchloropropane with Cs-K-Na in presence of 18-crown-6 gave 3-p-biphenylylpropylcesium as the initial product. Evidently this product exists in solution partly as a solvent-separated

ion pair, which underwent 1,3-proton shift to form 1-p-biphenylylpropylcesium, and partly as an intimate ion pair, which cyclized to form the more stable spiro anion; this interpretation is in accord with the acids isolated after carbonation of the reaction solution.

Reactions of 2-p-Biphenylyl-1-chloro-2-methylpropane with Alkali Metals

Though cyclopropyl and cyclobutyl rings have about the same total ring strain,[30] reaction of 1-p-biphenylyl-2-chloropropane with Cs-K-Na alloy in THF at -65° for one minute on carbonation gave a complex mixture of products containing only about 1% (if any) of spiro acid and much p-biphenylylethane.

In hope of stabilizing the possible spiro anion by methyl substitutions ("Thorpe-Ingold Effect") as in XXXIII, reaction of 2-p-biphenylyl-1-chloro-2-methylpropane with Cs-K-Na alloy was studied. When the



XXXIII

chloride was allowed to react with Cs-K-Na alloy in THF at -75° for about 70 seconds, the products from carbonation gave a complex mixture

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[30] J. Hine, "Structural Effects on Equilibria in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1975, p. 13.

of 7 carboxylic acids in which the four major more volatile products were identified as shown in Figure 6.

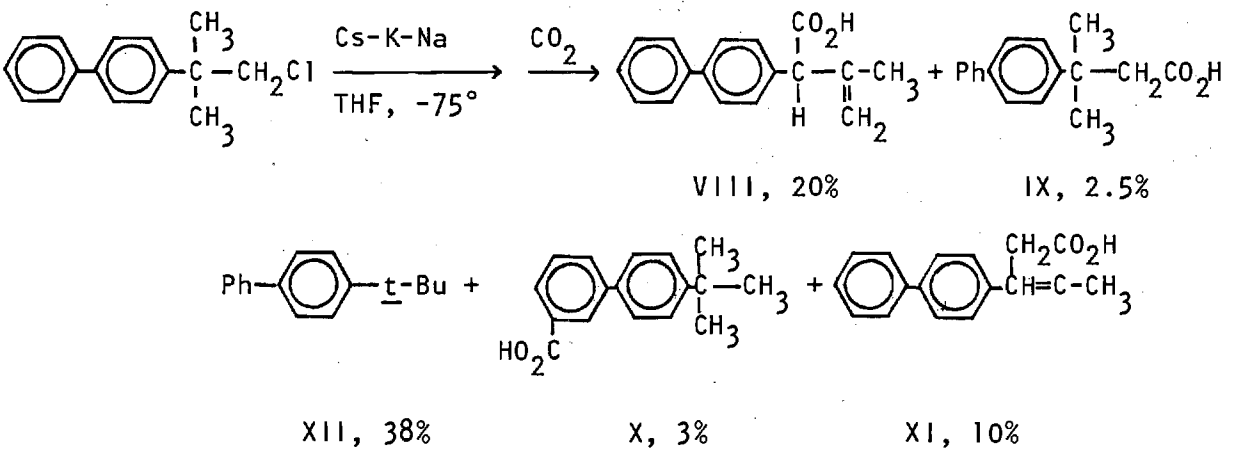


Figure 6. Reaction of 2-p-Biphenylyl-1-chloro-2-methylpropane with Cs-K-Na Alloy.

No product directly derived from the spiro anion was obtained. The olefinic acids VIII and XI are believed to be formed by α-elimination followed by proton abstraction from the olefin as shown in Figure 7. When the same reaction was run in presence of MeOH (a carbanion trapping agent, the product isolated showed about 13% of skeletal rearrangement. The rearranged products XIII and XVIII are believed to be formed by α-elimination followed by reduction of the olefin formed, as shown in Figure 7.

Reaction of lithium with 2-p-biphenylyl-1-chloro-2-methylpropane in THF at -75° gave the expected 2-methyl-2-p-biphenylyl-1-propyllithium (XXXVIII) along with some 10 to 15% of 2-methyl-1-p-biphenylyl-2-propyllithium (XXXIX) as shown in Figure 8. This rearrangement during reaction of the chloride with lithium metal has some precedent in the

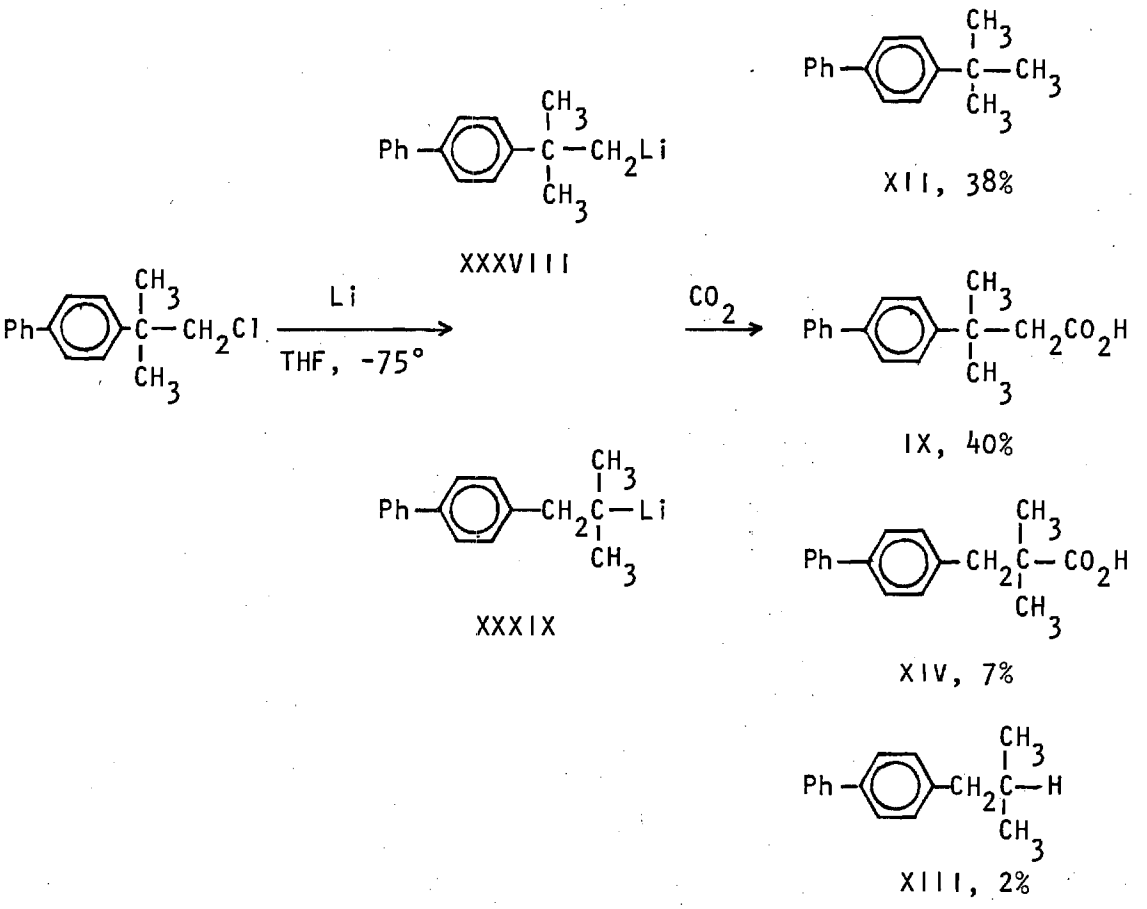


Figure 8. Reaction of 2-p-Biphenylyl-1-chloro-2-methylpropane with Lithium Metal.

equilibrium was not attained between these two organolithium compounds. When the chloride was allowed to react with lithium in THF at -75° in presence of t-BuOH, the same ratio of rearrangement was found in the products. These facts suggest that the rearranged organolithium was formed through a spirocyclic radical.

The organolithium reagent from the above reaction was treated with excess of KO-t-Bu in THF at -75° to give on carbonation ring metallation products as shown in Figure 9. This experiment demonstrates that in the time of the reaction with KO-t-Bu (10 minutes), compound XXXIII

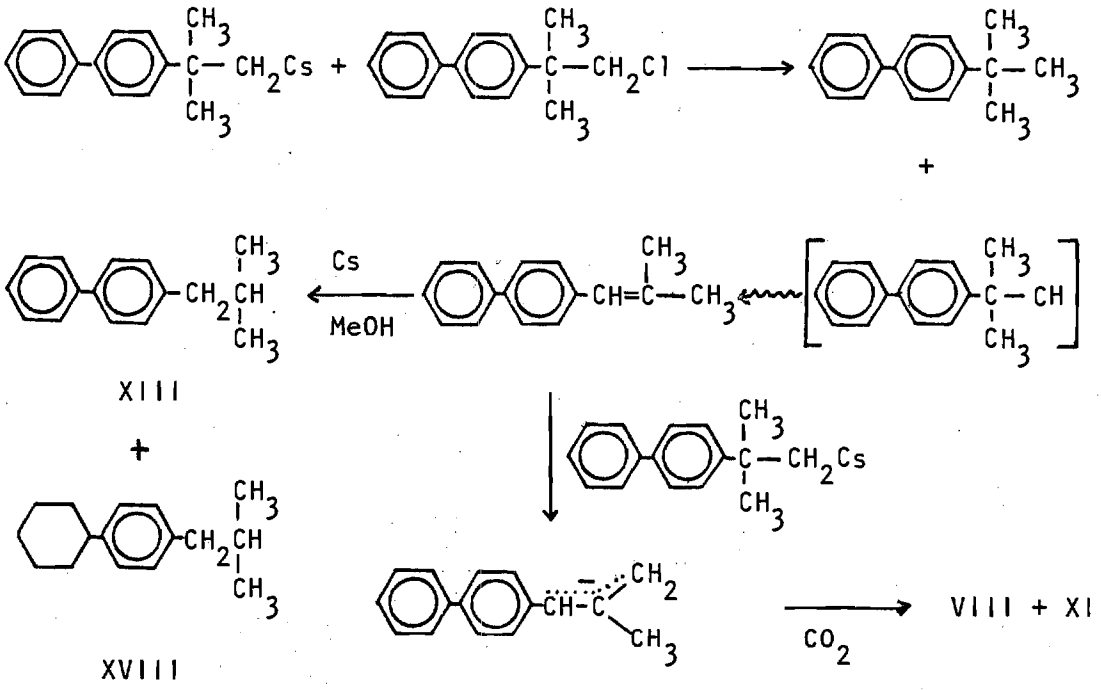
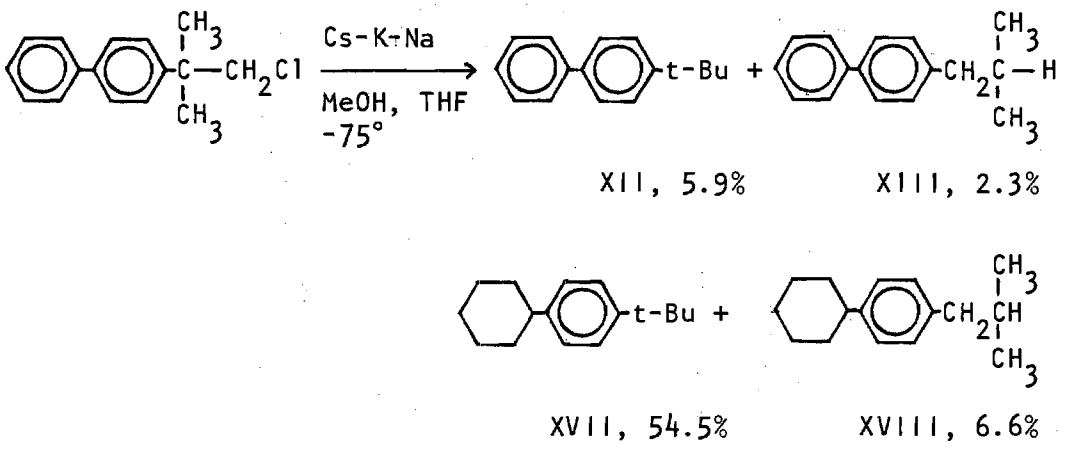


Figure 7. α-Elimination Reaction of 2-p-Biphenylyl-1-chloro-2-methylpropane.



reaction of neophyl chloride with lithium.[8] The amount of the rearranged products (XXXIX and 1-p-biphenylyl-2-methylpropane) did not increase with time or raising the temperature of the reaction mixture; evidently

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[8]E. Grovenstein, Jr. and Y. M. Cheng, Chem. Comm., 101 (1970).

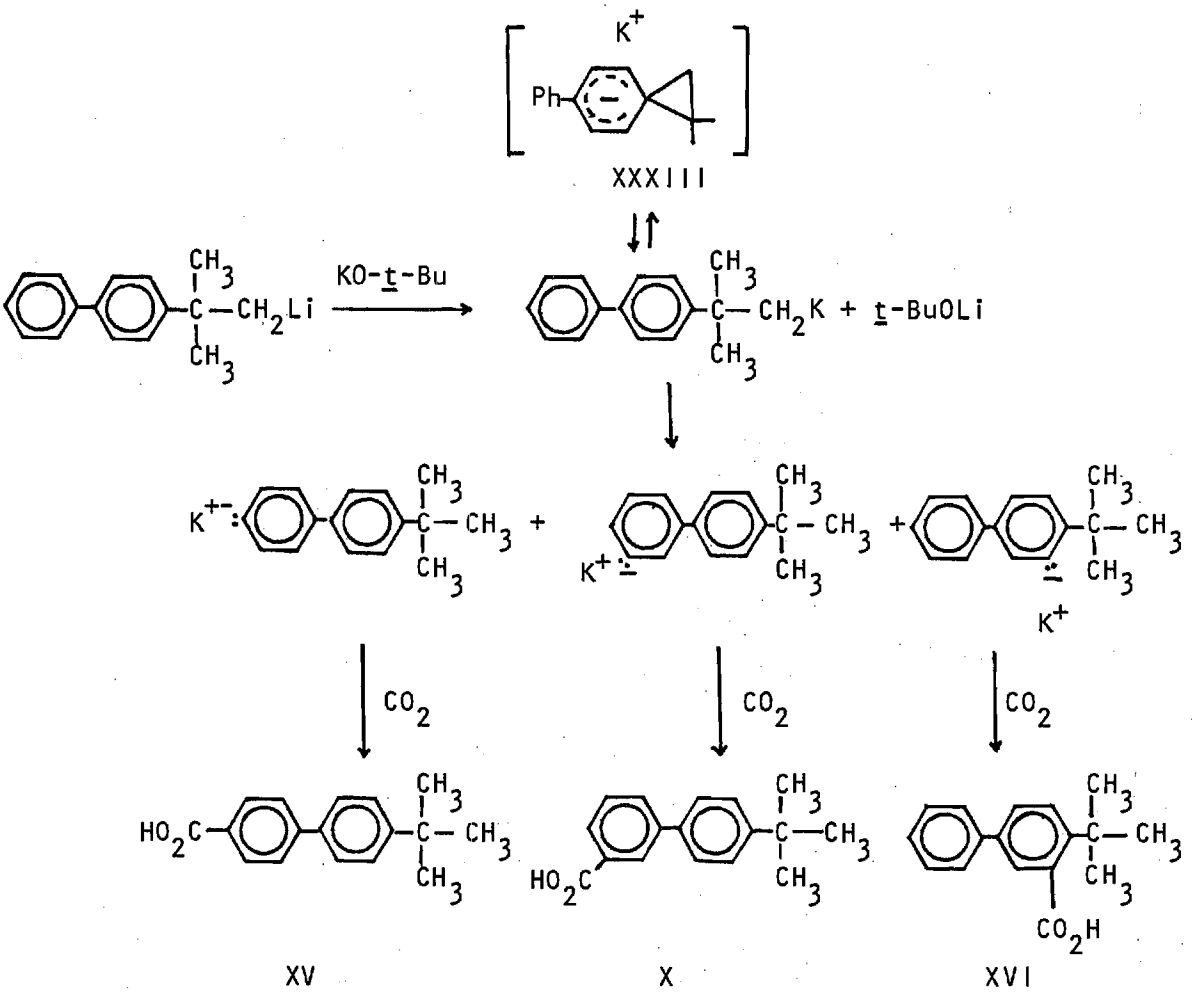


Figure 9. Reaction of 2-p-Biphenylyl-2-methylpropyllithium with t-BuOK.

was either not formed or, if it was formed, was unstable with respect to decomposition into the observed products. Two methyl groups in XXXIII do not provide adequate stabilization for detection of XXXIII by ordinary means.

Reactions of 1-p-Biphenylyl-2-chloro-2-methylpropane with Alkali Metals

Reaction of 1-p-biphenylyl-2-chloro-2-methylpropane with Cs-K-Na

alloy in THF at -75° gave on carbonation a complex mixture of products of which the major volatile products were identified as shown in Figure 10. The olefinic acids VIII and XI are believed to be formed by β-elimination followed by proton abstraction from the olefin

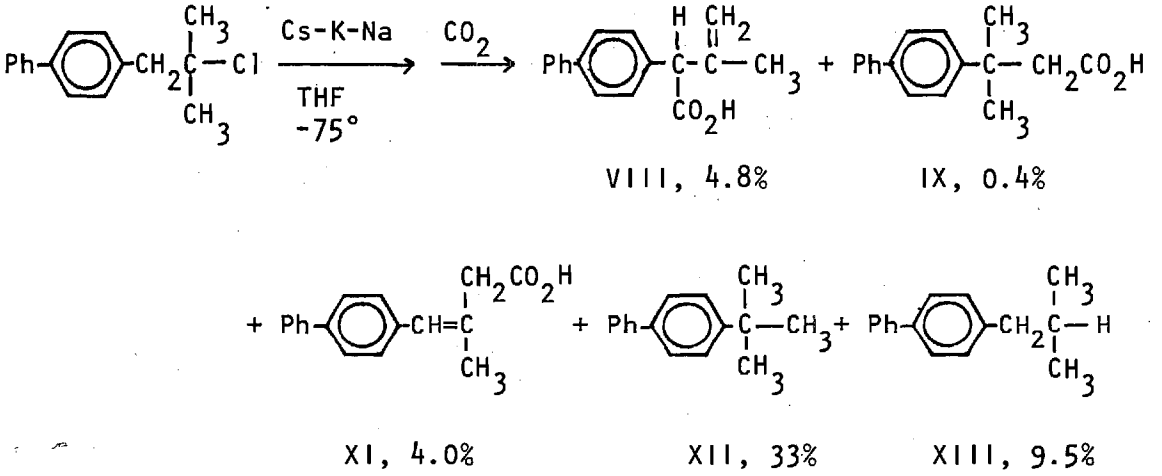


Figure 10. Reaction of 1-p-Biphenylyl-2-chloro-2-methylpropane with Cs-K-Na Alloy.

as shown in Figure 11. The considerable amount of t-butylbiphenyl migration has occurred. Speculatively the anion XXXIV is formed and cyclizes to XXXIII which in turn opens to XXXV probably because XXXV

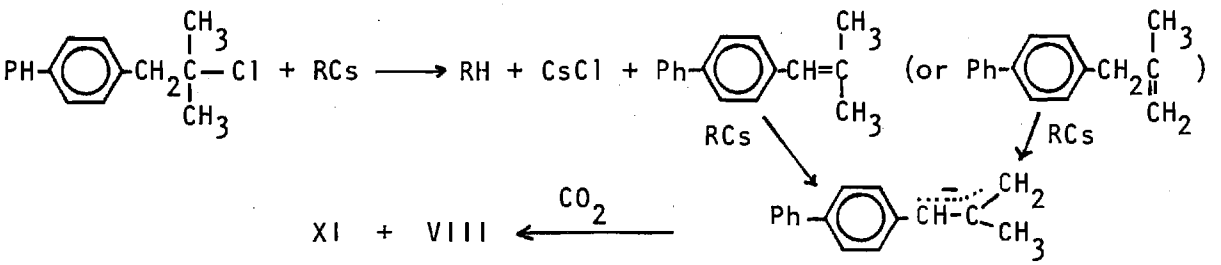
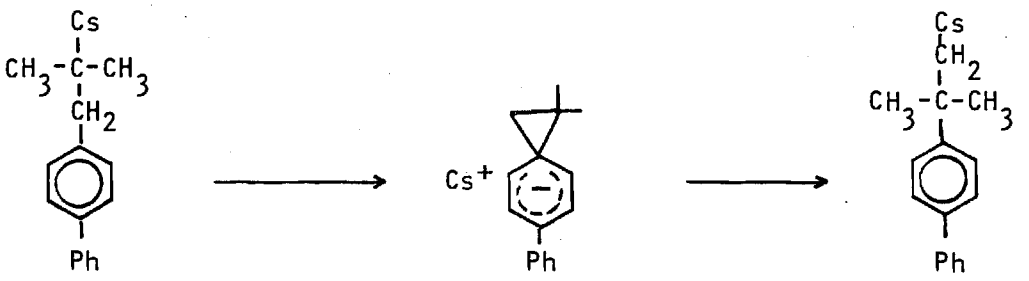


Figure 11. β-Elimination Reaction of 1-p-Biphenylyl-2-chloro-2-methylpropane.



XXXIV XXXIII XXXV

is more stable than XXXIV.

When the same reaction was run in THF at -75° in presence of methanol, the product isolated contained 1.3 mole % of t-butylbiphenyl, 19.4 mole % of 1-t-butyl-4-cyclohexylbenzene, 2.7 mole % of s-butylbiphenyl, and 38.7 mole % of 1-s-butyl-4-cyclohexylbenzene. Since methanol is a good carbanion trapping agent, the result of 67% of unrearranged product agrees well with the idea that it is mostly the carbanion (or an organocesium compound) which is undergoing rearrangement and which is trapped prior to rearrangement by addition of MeOH.

Reaction of lithium metal with 1-p-biphenylyl-2-chloro-2-methylpropane in THF at -75° gave on carbonation 18.8 mole % of t-butylbiphenyl, 23.8 mole % of isobutylbiphenyl, 29.5 mole % of 3-p-biphenylyl-2,2-dimethylpropanoic acid, and 7.4 mole % of 3-p-biphenylyl-3-methylbutanoic acid or 67% of the voltaile product was rearranged. When this reaction was repeated in presence of t-BuOH, 77% of unrearranged product was formed. A time study showed that in solution, there was no further rearrangement between the two organolithium compounds after they were formed. Thus the possible pathway for the formation of the rearranged organolithium compound could be partly via a spiro radical (which can

not be blocked by t-BuOH) and partly via a spiro anion in a solvent cage before an external lithium cation can attack the carbanion.

Reactions of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Alkali Metals

Since the Thorpe-Ingold effect is expected to be larger for four methyl groups than for two, the reactions of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na alloy were studied. Reaction of the chloride with Cs-K-Na alloy in THF at -75° for one minutes gave on carbonation 28 mole % of 1,1.2,2-tetramethyl-6-phenylspiro[2.5]octadiene-6-carboxylic acid (XXI), 7 mole % of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX), and 32 mole % of 2-p-biphenylyl-2,3-dimethylbutane (XXII) as listed in Table 4. The structure of XXI was fully confirmed by spectroscopic methods and by x-ray diffraction[31] upon a single crystal. These products are evidently formed according to Figure 12. When the reaction was repeated in presence of t-BuOH, only the open form product 2-p-biphenylyl-2,3-dimethylbutane was formed, so the open anion XXXIV should be the precursor of XXXV. When the organocesium reagent formed from this chloride was allowed to react with trimethylsilyl chloride or dimethyl sulfate, only open chain trimethylsilylation or methylation product in about 20 to 25% yield was formed. From the results of carbonation at different times the half-life of XXXV is about 22 minutes at -75° in THF. Interestingly the open form XXXIV seems to have the same half-life as XXXV. These results can

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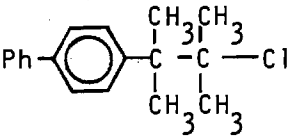
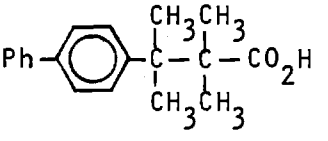
[31] J. A. Bertrand, E. Grovenstein, Jr., P.-C. Lu, D. VanDerveer, J. Amer. Chem. Soc., 98, 7835 (1976).

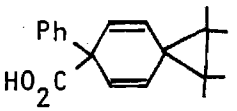
Table 4. Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Alkali Metals in THF at -75°

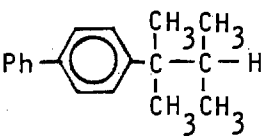
	Metal	Time	Mole % Yield Based on RCl* XIX	XX	XXI	XXII
1.	Li	50 min	2	37	0	41
2.	Li	50 min	9.6	34	0	22
		150 min	4.0	19.1	0	40.8
3.	$Li^+PhPh^{\cdot-}$	10 min	4	28	0	32
4.	Li	36 min	9.4	33.4	0	29
	+CsO-t-Bu	5 min	9.1	8.4	20.8	32.3
		12 min	8.7	7.1	16.6	34.6
5.	Cs-K-Na	50 sec	1.0	6.8	27.7	32.3
6.	Cs-K-Na	46 sec	0.9	7.3	26.2	30.3
7.	Cs-K-Na	5 min	65.2	3.8	6.2	14.7
		10 min	25.2	6.6	10.3	14.7
		16 min	4.4	14.4	22.0	22.4
		25 min	3.8	9.7	13.2	27.1
8.	Cs-K-Na	7 min	3.7	12.7	24.9	23.0
		15 min	1.2	9.9	19.5	20.4
		22 min	1.2	8.2	15.6	21.3
		29 min	0.8	5.6	12.8	21.3
9.	Cs-K-Na	22 sec	3.0	7.8	16.1	22.9
	+ LiBr	8 sec	2.2	24.1	0.10	23.9
	LiO-t-Bu					
10.	Cs-K-Na	35 sec	71.0			10.0
	+t-BuOH					

*

XIX. 

XX. 

XXI. 

XXII. 

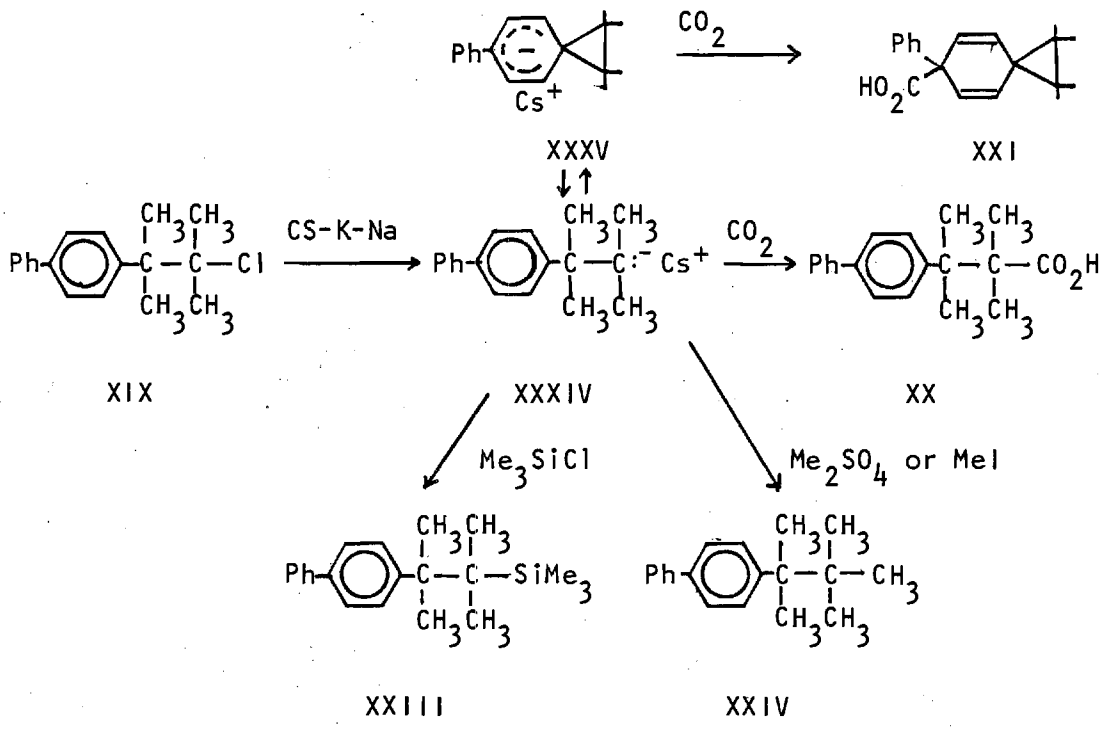


Figure 12. Reaction of 3-p-Biphenylyl-2-chloro-2,3-dimethylbutane with Cs-K-Na Alloy.

be understood if XXXV and XXXIV are in mobile equilibrium.

In a mobile equilibrium certain electrophilic reagents may attack one of the isomeric anions more readily than the other. Carbon dioxide appears to react instantaneously (or non-selectively) with the equilibrium mixture of the anions XXXIV and XXXV such that the product ratio of acids about (1:4) corresponds to the equilibrium composition. Trimethylsilyl chloride and dimethyl sulfate react with the anions readily but not instantaneously such that it appears to react considerably faster with the tertiary anion XXXIV than with the delocalized anion XXXV.

Attempts to react the mixture of anions XXXIV and XXXV in THF at -75° with trimethyloxonium tetrafluoroborate failed likely because of the low solubility of the oxonium salt in this solvent. At room

temperature the oxonium salt reacted with THF to form polymers.[35,36] When the same reaction was run in dimethyl ether as solvent, the organocesium compounds were formed in negligible yield possibly because they are insoluble in this solvent and coated the surface of the alkali metal.

Reaction of the same chloride XIX-d labeled with deuterium with Cs-K-Na alloy in THF at -75° and then decomposition of the reaction mixture with carbon dioxide, trimethylsilyl chloride, or water gave the products as summarized in Figure 13. In fact the major acids from

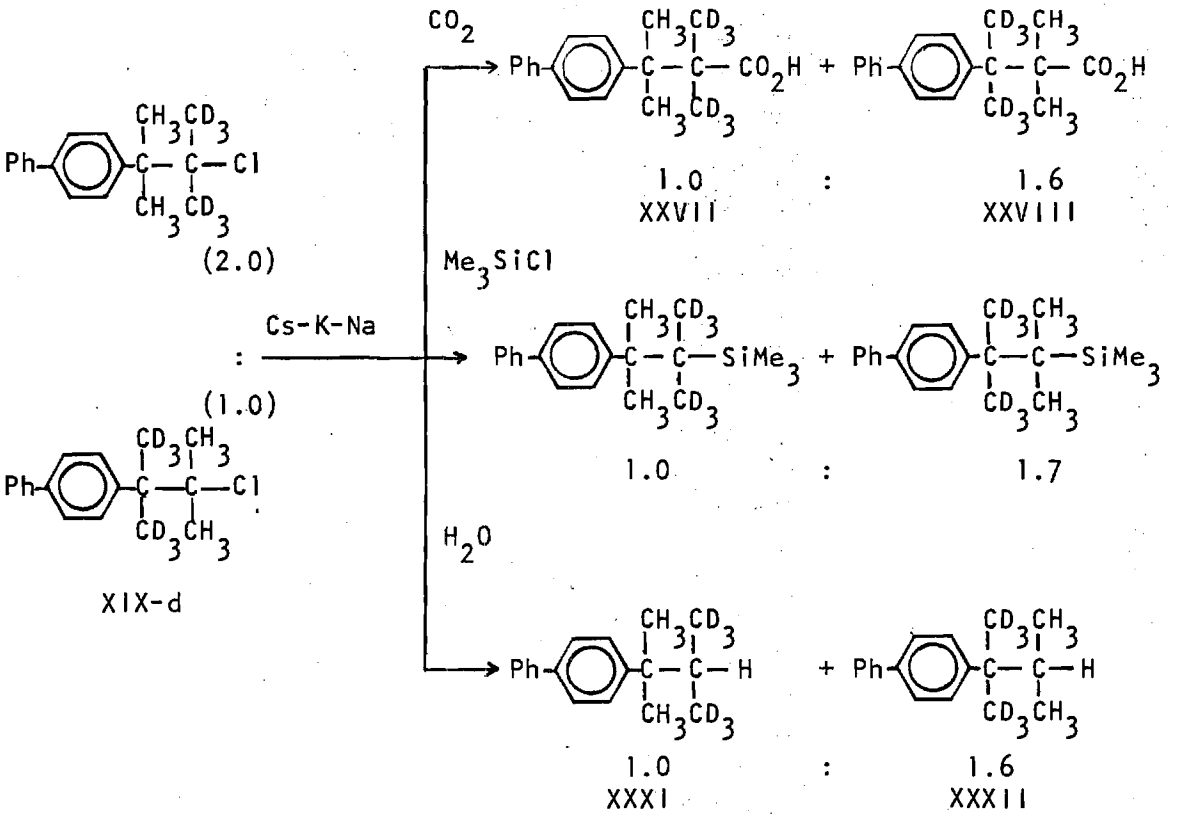


Figure 13. Reaction of 3-p-Biphenylyl-2-chloro-3-methyl-2-(methyl-d_3)butane-1,1,1-d_3 with Cs-K-Na Alloy.

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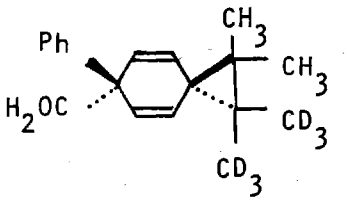
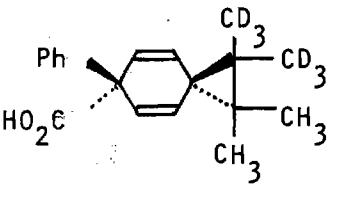
[35] H. Meerwein, D. Delfs, and H. Morschel, Angew Chem., 72, 927 (1960).

[36] G. A. Latremouille, G. T. Merrall, and A. M. Eastham, J. Amer. Chem. Soc., 82, 120 (1960).

carbonation were the mixture of spiro acids XXIX and XXX in some 20% yield (in a ratio of 1.0 : 1.0) whereas the open chain acid was produced

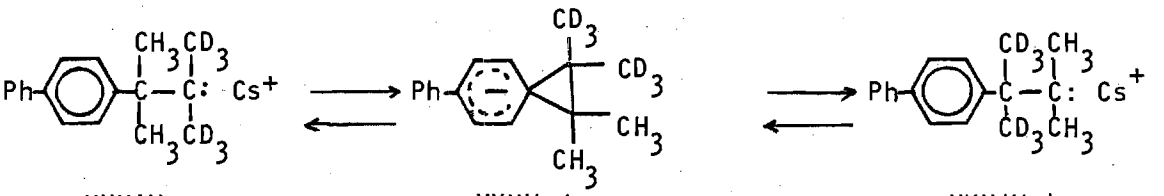


XXIX



XXX

in only 5 to 6% yield. The ratio of open chain aryl migration products in Figure 13 is about the ratio expected for equilibration of the position of the label in the corresponding anions. These labeling experiments confirm that the chloride XIX-d reacts with cesium to give the spiro anion XXXV-d which is in equilibrium with a lesser quantity of the open anions XXXIV-a and XXXIV-b:



	XXXIV-a		XXXV-d		XXXIV-b
Relative Ratio	1.0	:	10	:	1.7

Reaction of the chloride mixture XIX-d (starting with a deuterium labeling ratio of 1.2 : 1.0 with the isomeric form having deuteriums at methyl groups nearest to the chloride atom in excess) with Cs-K-Na alloy in THF at -75° gave on carbonation 27.6 mole % of the spirocyclic acid as the major product and 8.4 mole % of the open chain acids XXVII and XXVIII in a ratio of 1.0 : 1.6. This result that the isotopic product ratio is independent of the isotopic ratio in the starting chloride is in agreement with the conclusion that XXXIV-a, XXXV-d and

XXXIV-b are in ready equilibrium.

When lithium metal was allowed to react with the labeled chloride XIX-d with the same isomeric ratio of 2.0 : 1.0 as in Figure 13, only the open chain acids XXVII and XXVIII were obtained on carbonation with the deuterium labeling distribution of 1.0/1.6, having the rearranged form as the major product as with Cs-K-Na alloy in Figure 13. This isotopic distribution and the related results of carbonation, silylation and protonation from Cs-K-Na alloy reactions are expected for an equilibration of the position of the label in the corresponding open anion. That this secondary deuterium-isotope effect is large has good precedent in the reaction

$$(CD_3)_3N: + HN^+(CH_3)_3 \rightleftharpoons (CD_3)_3N^+H + :N(CH_3)_3$$

where $\Delta G°$ is reported to be -312 ± 30 cal/mole (evidently for the gas phase reaction,[32] $\Delta G°$ for this reaction in aqueous solution is -255 cal/mole at 0° to 50°.[33]) If $\Delta G°$ for the reaction (XXXV) $\rightleftarrows$ (XXXIV) is taken to be two thirds of the gas phase result for the reaction of $(CD_3)_3N$ with $HN(CH_3)_3$ because there are two thirds as many CD_3 groups present, then the ratio of XXXV to XXXIV at equilibrium at -75° is indeed calculated to be 1.7 : 1.0 essentially as found.

Reaction of the chloride XIX-d having the same deuterium labeling ratio of 2.0 to 1.0 as in Figure 13, with Cs-K-Na alloy in THF at -75° in presence of t-BuOH gave protonation products XXXI and XXXII in a

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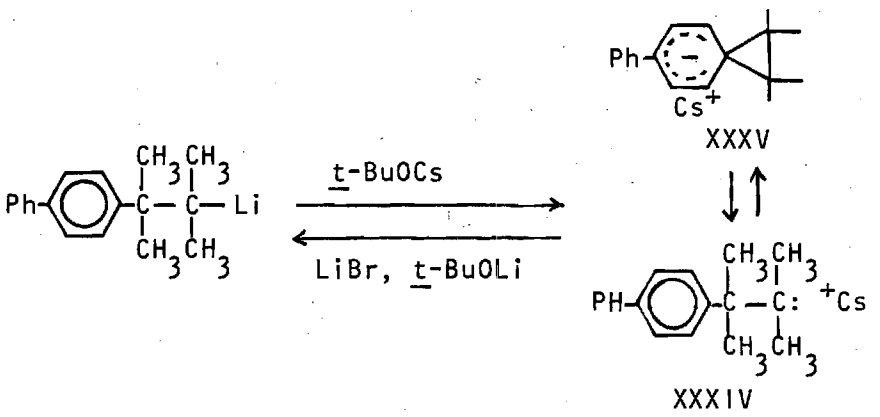
[32] J. F. Wolf, J. L. Delvin, D. J. DeFree, R. W. Taft, and W. F. Hehre, J. Amer. Chem. Soc., 98, 5097 (1976).

[33] D. Northcult and R. E. Robertson, J. Phys. Chem., 73, 1559 (1969).

ratio of 1.2 to 1.0. When the same reaction was repeated in presence of MeOH, the protonation products XXXI and XXXII were isolated in a ratio of 1.5 to 1.0 or nearly as in the starting chloride. This result shows that XXXIV, the precursor of XXXV, was moderately well trapped by t-BuOH but was better trapped by the stronger proton donor methanol before rearrangement.

Reaction of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane with lithium metal in THF at -75° gave only 33 mole % of the open acid XX on carbonation. The organolithium reagent from this reaction was treated with excess of CsO-t-Bu at -75° to give on carbonation 21 mole % of spirocyclic acid and 8 mole % of the open acid. Treatment of the equilibrium mixture of XXXIV and XXXV made from reaction of the chloride XIX with Cs-K-Na alloy in THF at -75° with excess of LiBr and LiO-t-Bu mixture gave on carbonation only the open acid. Evidently lithium cation prefers to interact with the localized anion since interaction can lead to the usual covalent organolithium compound. With cesium as counter cation, the equilibrium mixture of XXXIV and XXXV consists of about 1:4 ratio respectively of the anions (if the result



of carbonation can be relied upon to supply such information). Somewhat similar results were obtained by Maercker and Roberts[34] in their studies on cation effects in the cyclopropylcarbinyl-allylcarbinyl rearrangement.

[34] A. Maercker and J. D. Roberts, J. Amer. Chem. Soc., 88, 1742 (1966).

CHAPTER IV

RECOMMENDATIONS

It would be of interest to extend the study of p-biphenylyl migrations observed from the reaction of 3-p-biphenylyl-1-chloropropane with Cs-K-Na alloy to other related organic chlorides; 3-m-biphenylylpropyl chloride and 4-m-biphenylylbutyl chloride would be interesting examples. Reaction of p-methylbiphenyl or m-methylbiphenyl with simple olefins catalyzed by alkali metal reagents may also have some interesting aspects.

The possibility of using lithium biphenylide in THF for synthesis of organolithium compounds from alkyl halides would be an interesting topic to study. Similar possibilities of using potassium biphenylide or maybe cesium biphenylide in synthesis of organoalkali compounds would also be of interest.

APPENDIX A

X-RAY CRYSTALLOGRAPHY OF 1,1,2,2-TETRAMETHYL-6-PHENYLSPIRO[2.5]OCTA-4,7-DIENE-6-CARBOXYLIC ACID

The structure of this acid was determined by single-crystal x-ray diffraction analysis with aid of Professor J. A. Bertrand and Dr. D. VanDerveer. The acid crystallizes in the triclinic space group $P\bar{1}$ with a = 13.307(6), (note 1), b = 8.349(6), c = 10.217(2)Å, α = 90.75(4), β = 126.04(3), γ = 104.23(5)°, Z = 2, $d_c = d_m$ = 1.16 g cm^{-3}. The intensity data were measured with a Syntex $P2_1$ four-circle diffractometer, equipped with a graphite monochromator, using the θ-2θ scan technique. The structure, which was solved (note 2) by direct methods, was refined by least-squares methods (variables included a scale factor,

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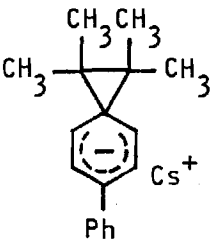
Note 1. Numbers in parentheses here and elsewhere indicate estimated standard deviations in the least significant digits.

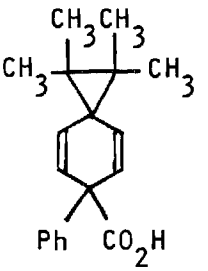
Note 2. All computations were carried out on the CDC Cyber 74 System. Standard programs utilized included: Germain, Main, and Woolfson's Multan, Zalkin's FORDAP, Iber's NUCLS modification of Busing, Martin and Levy's least-squares program, Busing and Levy's ORFFE, and Johnson's ORTEP. Scattering factors were taken from Cromer and Waber's tabulation (note 4) for carbon and oxygen; Stewart's hydrogen atom scattering factors (note 5) were used. Anomalous dispersion factors employed were those given by Cromer (note 6).

coordinates of all atoms, and anisotropic thermal parameters for all carbon and oxygen atoms; fixed isotropic thermal parameters of 4.0 were used for all hydrogen atoms) to convergence at R = 0.055 and R_w = 0.059 (256 variables, 2160 observations) (note 3). The structure is illustrated in Figure 14. Fractional coordinates, important bond distances, important bond angles, and observed and calculated structure factors are listed in Tables 5, 6, 7, and 8, respectively.

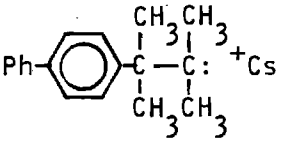
It was thought conceivable that x-ray analysis of this acid would reveal that steric compressions had been relieved on going into XXXV from the expected precursor 2-p-biphenylyl-1,1,2-trimethylpropylcesium (XXXIV). In fact the C(9)-C(9') or C(10)-C(10') distance in



XXXV



XXI



XXXIV

Note 3. $R = \Sigma||F_o| - |F_o||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|)^2]^{1/2}$.

Note 4. D. T. Cromer, and J. T. Waber, Acta Crystallogr., 18, 104 (1965).

Note 5. R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., 42, 3175 (1965).

Note 6. D. T. Cromer, Acta Crystallogr., 18, 17 (1965).

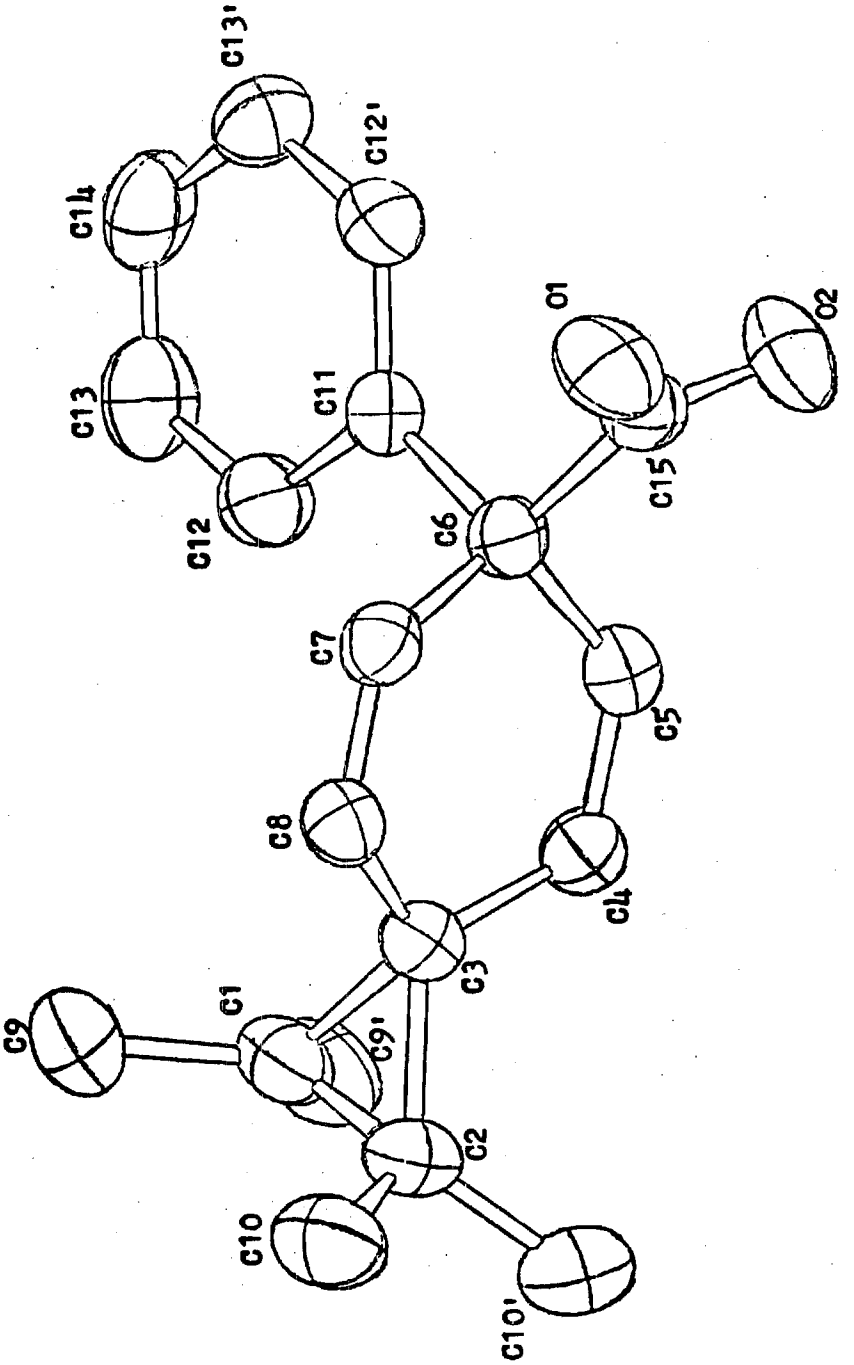


Figure 14. A perspective view of the molecular structure of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXI).

Table 5. Atomic Coordinates for the Acid XXI.

(a) Oxygen and Carbon Atoms

ATOM	10^4X/a	10^4Y/b	10^4Z/c
O1	3638(2)	3533(3)	3294(2)
O2	3901(2)	4275(2)	5580(2)
C1	-2600(3)	2738(4)	833(3)
C2	-2697(3)	898(4)	826(3)
C3	-1217(3)	2268(3)	1669(3)
C4	-176(3)	2606(3)	3474(3)
C5	1137(3)	2600(3)	4252(3)
C6	1722(2)	2185(3)	3378(3)
C7	748(3)	2268(3)	1577(3)
C8	-563(3)	2304(3)	818(3)
C9	-3177(3)	3370(5)	-763(4)
C9'	-2813(3)	3648(4)	1911(4)
C10	-2945(3)	-3(4)	1952(4)
C10'	-3318(3)	-289(4)	-724(4)
C11	1846(2)	387(3)	3553(3)
C12	3123(3)	58(3)	4501(3)
C12'	610(3)	-962(3)	2771(4)
C13	3141(4)	-1597(4)	4611(4)
C13'	646(4)	-2596(4)	2889(4)
C14	1916(4)	-2906(4)	3815(4)
C15	3188(3)	3426(3)	4136(3)

(b) Hydrogen Atoms

ATOM	10^3X/a	10^3Y/b	10^3Z/c
C4H1	-53(5)	286(5)	412(5)
C5H1	175(5)	278(5)	534(6)
C7H1	104(5)	212(5)	83(5)
C8H1	-112(5)	235(5)	-44(6)
C9H1	315(3)	-275(4)	156(4)
C9H2	422(4)	-317(4)	141(4)
C9H3	275(4)	-450(4)	49(4)
C9'H1	253(3)	-328(4)	-303(4)
C9'H2	374(4)	-356(4)	-133(4)
C9'H3	239(3)	-471(4)	-212(4)
C10H1	398(4)	60(4)	-127(4)
C10H2	253(3)	-58(4)	-301(4)
C10H3	260(3)	90(4)	-215(4)
C10'H1	315(3)	-20(4)	151(4)
C10'H2	298(3)	118(4)	52(4)
C10'H3	430(4)	77(4)	135(4)
C12H1	398(3)	94(4)	504(4)
C12'H1	-26(3)	-76(4)	207(4)
C13H1	401(3)	-185(3)	522(3)
C13'H1	-19(3)	-351(4)	235(4)
C14H1	193(3)	-400(4)	384(3)

Table 6. Bond Lengths for the Acid XXI.

Atoms	Distance(Å)	Atoms	Distance(Å)	Atoms	Distance(Å)
C1-C2	1.512	C6-C11	1.544	C13'-C14	1.368
C1-C3	1.569	C6-C15	1.524	C1-C9	1.508
C2-C3	1.553	C7-C8	1.330	C1-C9'	1.512
C3-C4	1.467	C11-C12	1.393	C2-C10	1.521
C3-C8	1.484	C11-C12'	1.391	C2-C10'	1.513
C4-C5	1.324	C12-C13	1.383	C15-01	1.263
C5-C6	1.520	C12'-C13'	1.379	C15-02	1.264
C6-C7	1.507	C13-C14	1.355		

Table 7. Bond Angles for the Acid XXI

Atoms	Angle (°)	Atoms	Angle (°)
C2-C1-C3	60.51	C5-C6-C7	109.90
C2-C1-C9	120.36	C5-C6-C11	108.08
C2-C1-C9'	121.42	C5-C6-C15	111.38
C3-C1-C9	117.53	C7-C6-C11	110.16
C3-C1-C9'	118.41	C7-C6-C15	108.27
C9-C1-C9'	110.45	C6-C7-C8	123.69
C1-C2-C3	61.56	C3-C8-C7	123.14
C1-C2-C10	119.92	C6-C11-C12	118.23
C1-C2-C10'	119.19	C6-C11-C12'	123.24
C3-C2-C10	118.79	C12-C11-C12'	118.18
C3-C2-C10'	118.32	C11-C12-C13	120.61
C10-C2-C10'	111.13	C11-C12'-C13'	121.17
C1-C3-C2	57.93	C12-C13-C14	121.37
C1-C3-C4	118.35	C11-C6-C15	109.09
C1-C3-C8	116.83	C12'-C13'-C14	119.28
C2-C3-C4	120.57	C13-C14-C13'	119.07
C2-C3-C8	119.77	C6-C15-01	118.37
C4-C3-C8	112.80	C6-C15-02	119.01
C3-C4-C5	123.54	01-C15-02	122.61
C4-C5-C6	123.55		

Table 8. Observed and Calculated Structure Amplitudes for Acid XXI

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
	H=-14			5	5	3	3	5	8	3	2	2	5	11	12
				5	6	1	1	5	9	3	3	2	6	2	1
0	6	2	2	5	8	4	3	6	2	6	6	2	7	6	6
0	7	1	2	5	9	1	1	6	4	1	1	2	8	2	3
1	6	5	5	6	4	3	3	6	5	6	6	2	10	4	4
1	8	2	2	6	7	3	3	6	7	3	3	3	1	4	4
1	9	5	5					7	3	1	1	3	2	9	9
2	6	3	3		H=-12			7	4	2	2	3	4	1	1
2	8	2	2					7	5	2	2	3	6	10	10
2	9	1	1	-3	5	1	1	7	6	4	4	3	7	1	1
3	4	3	3	-3	6	8	8	7	7	7	6	3	8	6	6
3	6	2	2	-3	7	2	2					3	9	4	3
3	8	1	1	-3	8	1	1		H=-11			3	10	1	2
3	9	6	5	-2	4	1	1					4	1	4	4
4	5	2	2	-2	5	8	8	-4	4	2	2	4	2	6	7
4	6	6	6	-2	7	1	1	-4	5	6	5	4	3	5	5
4	7	2	1	-2	8	1	1	-4	6	2	2	4	4	8	8
4	8	4	4	-1	5	2	3	-4	7	4	4	4	5	8	8
5	6	2	1	-1	6	6	6	-4	9	2	2	4	7	2	2
5	7	4	3	-1	7	4	4	-3	3	2	3	4	8	6	6
				-1	9	1	1	-3	5	2	2	4	9	3	3
	H=-13			-1	10	1	1	-3	6	2	2	4	10	1	1
				0	3	2	2	-3	7	4	4	5	1	4	4
-2	6	3	2	0	4	1	1	-3	9	2	2	5	3	2	1
-2	7	6	6	0	5	8	8	-3	10	1	2	5	4	5	5
-2	8	3	3	0	7	2	2	-2	3	3	3	5	5	6	5
-1	4	1	1	0	10	2	2	-2	5	4	4	5	6	5	5
-1	5	4	3	1	2	1	2	-2	6	3	2	5	7	4	4
-1	6	5	5	1	5	10	11	-2	8	2	2	5	8	3	2
-1	9	5	5	1	6	5	5	-2	9	6	6	5	9	2	2
0	5	2	1	1	10	1	1	-1	1	2	2	6	2	3	2
0	6	4	4	2	1	3	2	-1	2	5	5	6	3	3	3
0	7	6	6	2	5	2	2	-1	3	2	2	6	4	1	1
0	8	2	2	2	6	3	2	-1	4	3	3	6	5	3	3
0	9	1	1	2	7	3	3	-1	5	4	4	6	6	3	3
0	10	4	4	2	8	2	1	-1	6	4	4	6	8	6	5
1	3	2	1	2	9	1	1	-1	8	3	2	7	1	4	4
1	4	3	3	3	2	2	2	-1	10	2	1	7	4	4	4
1	5	5	5	3	3	1	1	-1	11	3	3	7	5	2	2
1	7	8	8	3	4	1	1	0	1	4	4	7	8	6	5
1	8	8	8	3	5	9	9	0	2	4	5	8	3	1	1
1	9	5	5	3	6	2	2	0	3	10	11	8	5	4	3
2	3	1	2	3	8	3	2	0	4	2	2				
2	4	1	2	3	9	1	1	0	5	4	4		H=-10		
2	5	3	3	3	10	3	3	0	6	9	9				
2	8	5	5	3	11	2	1	0	7	16	16	-5	5	5	5
2	9	3	3	4	2	4	4	1	1	4	4	-5	6	1	2
2	10	2	2	4	3	3	3	1	3	6	5	-5	7	3	3
3	5	2	2	4	6	6	6	1	4	8	8	-4	2	5	4
3	10	2	2	4	10	2	2	1	6	15	15	-4	3	3	3
4	3	2	2	5	1	2	2	1	7	4	4	-4	5	8	9
4	4	8	8	5	3	4	4	1	8	4	4	-4	6	1	2
4	6	2	2	5	4	2	2	1	10	5	6	-4	7	3	3
4	7	1	1	5	5	4	4	2	1	3	3	-4	8	1	0
4	9	3	2	5	6	1	1	2	3	6	6	-4	9	1	1
5	3	2	2	5	7	2	1	2	4	2	2	-3	2	7	7

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-3	5	5	5	3	8	3	4	-3	8	1	1	4	5	13	14
-3	6	3	3	3	9	7	7	-3	10	2	2	4	6	3	3
-3	7	2	2	4	1	11	11	-2	1	8	9	4	7	1	0
-3	8	2	2	4	2	1	1	-2	2	5	5	4	8	1	1
-3	9	2	1	4	3	3	3	-2	4	3	2	4	9	4	5
-2	1	4	4	4	4	5	5	-2	5	16	17	4	11	2	1
-2	2	2	2	4	5	10	10	-2	6	8	8	5	2	2	2
-2	3	4	4	4	6	1	1	-2	7	7	7	5	4	16	16
-2	5	1	1	4	8	3	3	-2	8	4	4	5	5	3	3
-2	7	7	7	4	9	3	3	-2	9	2	2	5	6	3	3
-2	8	1	1	4	11	2	2	-2	10	4	4	5	7	2	2
-2	9	4	3	5	2	5	5	-1	3	10	11	5	8	1	0
-1	1	3	3	5	3	1	1	-1	4	13	14	5	9	6	6
-1	2	3	4	5	4	4	4	-1	5	7	6	5	10	3	3
-1	3	3	3	5	6	7	7	-1	7	2	2	6	1	10	10
-1	4	5	5	5	8	4	4	-1	8	9	9	6	2	3	3
-1	5	1	1	6	1	5	5	-1	9	2	2	6	3	2	3
-1	6	18	20	6	2	1	2	-1	11	3	3	6	4	8	8
-1	7	3	3	6	3	6	6	-1	12	3	2	6	5	18	17
-1	8	1	1	6	4	5	5	0	1	8	9	6	6	4	4
-1	9	4	4	6	5	1	2	0	2	5	5	6	8	5	5
-1	10	6	7	6	6	8	8	0	3	15	14	6	9	2	2
0	1	9	10	6	7	2	2	0	5	5	5	7	1	3	4
0	2	9	9	7	2	1	1	0	7	6	6	7	3	4	4
0	3	7	6	7	3	1	1	0	8	2	2	7	4	3	4
0	4	7	8	7	4	4	4	0	9	3	4	7	5	6	6
0	5	34	34	7	5	2	2	0	10	4	4	7	6	1	1
0	7	2	2	7	6	2	2	1	1	7	7	7	7	3	2
0	8	4	3	7	7	5	5	1	2	17	18	7	8	3	2
0	9	7	8	8	1	2	1	1	4	14	14	8	1	5	5
0	10	4	4	8	2	1	1	1	5	1	1	8	2	2	1
0	11	2	2	8	4	4	4	1	6	7	7	8	3	4	4
0	12	3	3	8	5	4	4	1	8	6	8	8	4	4	4
1	2	7	8	8	6	3	3	1	9	1	1	8	5	2	2
1	3	7	7					1	10	1	2	8	7	2	1
1	4	12	12		H=	-9		1	12	7	6	9	3	3	3
1	5	7	7					2	1	7	7	9	4	3	3
1	6	10	11	-6	5	4	4	2	2	2	1				
1	8	9	9	-6	7	2	2	2	3	10	9		H=	-8	
1	9	2	3	-5	2	1	1	2	4	2	2				
1	10	3	4	-5	5	1	2	2	5	9	9	-6	3	1	1
1	12	6	5	-5	6	3	3	2	6	6	5	-6	5	2	2
2	1	6	7	-5	7	2	2	2	9	2	2	-6	7	1	1
2	2	4	5	-5	9	4	3	2	11	2	2	-6	8	3	3
2	3	2	1	-4	1	3	3	3	1	2	2	-5	2	2	2
2	4	2	2	-4	2	3	4	3	2	4	4	-5	4	2	1
2	5	18	18	-4	3	3	4	3	3	8	8	-5	6	3	3
2	6	5	5	-4	5	7	6	3	4	9	8	-5	7	2	2
2	7	2	2	-4	6	3	2	3	5	15	14	-5	8	8	8
2	8	4	4	-4	7	3	3	3	7	8	8	-5	9	7	8
2	9	4	5	-4	8	2	2	3	8	3	2	-5	10	2	2
3	1	6	6	-3	2	6	7	3	10	2	2	-4	4	5	5
3	2	3	3	-3	4	2	2	4	1	4	4	-4	5	2	2
3	4	13	14	-3	5	1	1	4	2	1	1	-4	6	8	8
3	5	8	8	-3	6	13	13	4	3	3	3	-4	7	3	3
3	6	3	3	-3	7	6	7	4	4	4	4	-4	8	3	3

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-4	9	1	1	3	4	6	6	-5	6	8	9	2	2	5	4
-3	1	2	1	3	5	5	5	-5	7	16	16	2	3	15	14
-3	4	7	7	3	7	2	1	-5	8	3	3	2	4	22	22
-3	5	8	9	3	8	3	3	-5	9	2	2	2	5	7	7
-3	7	6	6	3	9	7	7	-5	10	7	7	2	6	1	1
-3	8	1	1	3	10	3	2	-4	2	4	5	2	7	2	2
-3	9	4	4	4	1	3	3	-4	3	4	4	2	8	7	7
-2	1	2	1	4	2	2	2	-4	4	4	4	3	1	9	9
-2	2	2	2	4	3	10	10	-4	6	9	9	3	2	11	11
-2	4	7	7	4	4	5	5	-4	9	4	4	3	3	6	7
-2	5	1	1	4	5	3	3	-4	10	5	5	3	4	4	5
-2	6	17	16	4	7	6	6	-3	1	1	2	3	5	6	6
-2	8	8	9	4	8	4	3	-3	2	7	7	3	7	8	7
-2	9	3	3	4	9	2	1	-3	3	3	3	3	9	2	2
-2	10	1	1	4	10	2	2	-3	4	7	6	3	10	2	2
-1	1	15	15	5	1	3	4	-3	5	11	11	4	1	12	13
-1	2	9	9	5	2	8	8	-3	6	2	2	4	2	4	4
-1	3	1	1	5	3	5	5	-3	7	3	3	4	3	5	5
-1	4	4	4	5	4	13	12	-3	9	4	4	4	4	6	4
-1	6	11	11	5	5	4	3	-3	10	4	3	4	5	11	11
-1	7	2	2	5	6	1	2	-2	1	6	6	4	7	5	5
-1	9	4	3	5	7	8	8	-2	2	12	12	4	8	6	6
-1	10	4	4	5	8	5	5	-2	3	1	1	4	9	8	9
-1	11	2	2	5	10	2	1	-2	4	16	15	4	10	1	1
-1	12	5	5	6	1	10	10	-2	5	7	7	5	2	5	5
0	1	9	9	6	2	13	13	-2	6	9	9	5	3	2	2
0	2	4	4	6	3	19	19	-2	7	8	8	5	4	7	6
0	3	14	13	6	4	5	5	-2	8	4	4	5	5	2	1
0	4	3	3	6	5	6	5	-2	9	3	3	5	6	7	7
0	5	4	4	6	6	4	4	-2	10	8	8	6	1	3	4
0	6	2	2	6	7	3	3	-2	11	5	5	6	2	9	9
0	7	2	2	6	8	1	1	-1	2	1	0	6	3	9	9
0	8	2	1	7	1	5	6	-1	4	8	8	6	4	1	2
0	9	12	12	7	3	1	2	-1	5	2	0	6	5	7	7
0	10	2	2	7	4	3	3	-1	6	2	1	7	1	1	2
1	1	2	2	7	6	1	1	-1	8	6	6	7	2	2	2
1	2	5	6	7	7	1	1	-1	9	7	7	7	3	5	6
1	4	5	5	8	1	3	3	-1	10	4	4	7	5	4	4
1	6	2	2	8	3	3	3	0	1	17	19	7	6	3	2
1	7	2	2	8	5	2	3	0	2	1	1	7	8	2	2
1	8	8	9	9	2	1	1	0	3	6	6	8	2	2	2
1	9	1	1	9	4	3	3	0	5	20	20	8	3	4	4
1	10	10	10					0	6	4	5	8	5	1	1
1	11	4	4		H=	-7		0	7	3	3	8	7	2	2
2	1	1	2					0	8	8	7	9	2	2	1
2	2	5	5	-7	4	2	2	0	9	3	3	9	3	2	2
2	3	6	5	-7	7	1	1	0	10	5	5	9	5	2	2
2	4	14	14	-6	2	2	2	1	1	3	3				
2	5	13	14	-6	3	2	2	1	3	1	1		H=	-6	
2	6	11	11	-6	6	3	3	1	4	7	8				
2	8	1	1	-6	7	3	3	1	5	3	4	-7	1	2	1
2	10	3	3	-6	9	2	3	1	6	4	3	-7	2	5	4
2	11	5	5	-5	1	2	2	1	8	9	9	-7	3	3	3
3	1	7	8	-5	2	11	11	1	9	6	7	-7	5	2	2
3	2	7	7	-5	4	3	3	1	11	3	3	-7	6	6	6
3	3	7	7	-5	5	5	5	2	1	2	3	-7	7	5	4

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-6	1	2	1	0	5	21	21	7	4	5	5	-2	5	2	2
-6	4	4	4	0	6	20	20	7	5	1	1	-2	6	12	12
-6	5	7	7	0	7	7	8	7	6	2	1	-2	7	3	3
-6	6	4	4	0	8	4	4	7	7	3	3	-2	8	5	4
-6	7	4	4	0	9	6	6	7	8	2	1	-2	9	7	7
-6	8	11	11	0	10	9	9	8	1	1	1	-2	10	2	2
-5	2	3	4	1	1	6	6	8	3	3	2	-1	1	3	3
-5	3	1	1	1	2	33	32	8	6	2	2	-1	2	27	25
-5	4	2	3	1	4	8	8	9	3	2	2	-1	3	8	7
-5	5	16	15	1	5	13	14	9	4	2	2	-1	4	15	15
-5	6	2	2	1	6	16	18					-1	5	27	26
-5	7	3	3	1	7	12	11		H=	-5		-1	6	7	7
-5	8	8	8	1	8	5	6					-1	7	5	5
-5	9	8	8	1	10	12	12	-8	3	1	1	-1	8	4	4
-4	1	7	7	2	1	9	8	-8	5	3	2	-1	9	8	8
-4	2	3	3	2	2	6	5	-7	1	2	2	-1	10	5	5
-4	3	5	4	2	4	10	10	-7	4	2	2	-1	11	1	1
-4	4	5	5	2	5	6	6	-7	5	5	5	0	1	46	46
-4	6	3	4	2	6	7	7	-7	6	2	2	0	2	1	1
-4	7	4	4	2	8	2	2	-7	7	2	2	0	3	1	1
-4	8	7	8	2	9	9	9	-6	2	5	6	0	4	32	32
-4	9	5	5	2	10	2	2	-6	3	12	12	0	5	6	5
-4	10	6	6	3	1	8	7	-6	4	2	3	0	6	2	1
-4	11	3	2	3	2	4	4	-6	5	5	5	0	7	8	8
-3	1	12	13	3	3	6	6	-6	6	8	8	0	8	30	31
-3	2	1	1	3	4	3	2	-6	7	7	7	0	9	14	14
-3	3	2	1	3	5	9	8	-6	8	5	5	0	10	4	4
-3	4	4	4	3	6	3	3	-5	1	2	2	0	11	3	2
-3	5	2	2	3	8	12	12	-5	2	4	4	1	1	22	22
-3	6	5	6	3	9	4	3	-5	3	7	7	1	3	14	14
-3	7	4	4	3	11	4	3	-5	4	2	2	1	4	28	29
-3	9	7	7	4	1	1	2	-5	5	19	19	1	5	13	14
-3	10	4	4	4	2	1	1	-5	6	2	3	1	6	15	14
-2	1	8	8	4	3	10	9	-5	7	7	7	1	7	3	3
-2	3	7	8	4	4	4	5	-5	9	4	4	1	8	26	27
-2	4	16	15	4	5	7	7	-4	1	1	1	1	9	12	12
-2	5	7	6	4	6	7	7	-4	2	1	1	1	11	3	2
-2	6	10	9	4	7	14	14	-4	3	2	2	2	1	13	14
-2	7	4	4	4	8	3	3	-4	4	8	7	2	2	14	14
-2	8	13	14	4	9	3	3	-4	5	11	12	2	3	10	9
-2	9	3	4	4	10	1	2	-4	6	3	2	2	4	31	29
-2	11	2	1	5	2	12	11	-4	7	1	1	2	5	7	8
-1	1	3	3	5	3	4	4	-4	8	9	9	2	6	7	7
-1	2	13	12	5	4	8	9	-3	1	9	9	2	7	8	9
-1	3	4	3	5	5	11	11	-3	3	3	3	2	8	10	11
-1	4	5	5	5	6	3	2	-3	4	9	9	2	9	3	3
-1	5	3	1	5	8	6	5	-3	5	3	3	2	11	3	3
-1	6	9	9	5	9	2	2	-3	6	11	11	3	1	22	22
-1	7	1	1	6	1	5	5	-3	7	1	2	3	2	2	2
-1	8	3	2	6	2	2	2	-3	8	13	13	3	3	10	9
-1	9	4	3	6	3	6	7	-3	9	2	2	3	4	3	3
-1	10	4	3	6	4	9	9	-3	10	6	5	3	7	3	4
0	1	2	1	6	7	4	4	-2	1	15	14	3	9	2	3
0	2	13	12	6	9	2	2	-2	2	19	18	4	1	5	4
0	3	8	9	7	1	6	5	-2	3	11	10	4	3	6	6
0	4	2	2	7	3	6	6	-2	4	9	10	4	4	3	3

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
4	5	1	2	-4	1	1	0	1	11	4	3	-7	1	2	2
4	6	2	1	-4	2	9	8	2	1	22	22	-7	2	6	6
4	7	7	7	-4	3	3	3	2	2	9	8	-7	3	6	6
4	8	9	9	-4	5	11	11	2	3	7	6	-7	4	1	1
5	1	3	4	-4	7	4	4	2	4	1	0	-7	5	5	5
5	2	6	6	-4	8	8	8	2	5	21	20	-7	6	3	2
5	3	18	17	-4	9	1	1	2	6	6	6	-7	7	3	3
5	4	9	9	-4	10	2	2	2	7	3	3	-7	8	1	2
5	5	8	8	-3	2	1	2	2	8	8	8	-6	1	9	8
5	6	2	2	-3	4	6	6	2	9	2	2	-6	2	14	13
5	7	5	4	-3	5	26	26	3	1	2	3	-6	3	5	5
5	8	3	2	-3	6	8	8	3	2	2	2	-6	4	8	8
6	1	5	6	-3	7	5	5	3	3	3	4	-6	5	7	7
6	2	7	7	-3	8	8	8	3	4	36	35	-6	6	5	5
6	3	3	3	-3	9	11	11	3	6	1	1	-6	8	5	5
6	4	1	1	-3	11	3	1	3	7	6	7	-5	1	12	12
6	5	2	1	-2	1	16	16	3	8	6	6	-5	2	7	7
6	7	4	3	-2	2	20	19	4	1	26	26	-5	3	3	3
7	1	2	1	-2	3	17	16	4	2	8	9	-5	4	3	3
7	2	6	5	-2	4	23	22	4	3	7	6	-5	5	2	1
7	3	1	1	-2	5	7	7	4	4	16	16	-5	6	7	8
7	4	4	4	-2	6	5	5	4	5	6	6	-5	7	2	3
7	6	2	2	-2	7	3	3	4	6	8	7	-5	8	3	3
8	1	1	2	-2	8	7	7	4	8	2	3	-5	9	3	3
8	2	2	2	-2	9	2	2	4	9	3	3	-4	1	3	3
8	3	3	3	-2	11	2	2	5	1	3	3	-4	2	8	7
8	4	3	3	-1	1	14	13	5	2	9	9	-4	3	3	3
8	5	1	2	-1	2	13	12	5	3	6	6	-4	4	2	1
9	2	4	4	-1	3	17	15	5	4	4	5	-4	5	6	7
9	3	1	2	-1	4	15	15	5	5	7	7	-4	6	4	4
				-1	5	4	3	5	7	1	1	-4	7	7	8
	H=	-4		-1	6	11	11	5	8	3	4	-4	8	5	4
				-1	7	10	9	6	1	2	2	-3	1	11	12
-8	2	3	2	-1	8	12	12	6	3	3	3	-3	2	2	1
-8	7	2	2	-1	9	8	7	6	4	11	11	-3	3	5	6
-7	2	2	2	-1	10	5	4	6	5	3	3	-3	4	5	5
-7	4	6	7	-1	11	7	6	6	6	2	2	-3	5	5	4
-7	5	5	5	0	1	27	26	6	7	9	10	-3	6	4	4
-7	6	2	2	0	2	14	13	6	8	7	7	-3	7	11	11
-6	1	10	9	0	3	15	15	7	1	2	2	-3	8	3	3
-6	2	1	1	0	4	6	5	7	2	5	4	-3	9	6	6
-6	3	6	6	0	5	29	29	7	3	6	6	-3	10	2	2
-6	4	5	4	0	6	35	34	7	4	4	4	-2	1	33	32
-6	5	14	14	0	7	9	9	8	2	2	2	-2	2	33	32
-6	6	3	2	0	8	15	15	8	3	2	2	-2	3	15	14
-6	7	3	2	0	9	2	2	8	6	2	1	-2	4	16	16
-6	8	3	3	0	10	4	4	9	1	2	2	-2	5	18	18
-5	1	7	7	0	11	2	1	9	3	2	2	-2	6	7	7
-5	2	10	9	1	1	15	16					-2	7	1	1
-5	3	19	20	1	2	1	1		H=	-3		-2	8	11	10
-5	4	1	1	1	3	15	14					-2	9	1	2
-5	5	1	1	1	4	26	26	-8	1	3	3	-2	10	4	4
-5	6	3	3	1	5	19	21	-8	2	2	3	-2	11	1	1
-5	8	2	2	1	6	11	12	-8	5	1	1	-1	1	23	22
-5	9	4	4	1	7	14	14	-8	6	5	5	-1	2	11	11
-5	10	2	1	1	8	9	9	-8	7	2	2	-1	3	7	7

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-1	4	29	29	6	1	4	4	-3	1	43	42	3	5	7	7
-1	5	3	5	6	2	7	7	-3	2	17	17	3	6	10	11
-1	6	2	2	6	3	5	5	-3	3	20	20	3	7	5	5
-1	7	5	6	6	4	1	1	-3	4	1	1	3	8	4	4
-1	8	2	2	6	5	7	7	-3	5	4	4	4	1	28	27
-1	9	7	7	6	6	8	7	-3	6	2	1	4	2	4	4
-1	11	2	2	6	7	4	4	-3	7	8	8	4	3	1	0
0	1	39	38	6	8	4	4	-3	8	1	1	4	4	2	3
0	2	38	38	7	1	3	3	-3	9	6	6	4	5	2	0
0	3	42	43	7	4	9	8	-3	10	3	2	4	6	2	2
0	4	25	24	7	5	6	6	-2	1	31	30	5	2	1	1
0	5	16	16	7	6	6	6	-2	2	9	8	5	3	6	7
0	6	13	13	8	2	3	3	-2	3	17	17	5	4	7	6
0	7	2	1	8	3	3	3	-2	4	15	14	5	5	4	2
0	8	6	6	8	4	4	4	-2	5	5	6	5	6	1	2
0	9	3	2	8	5	2	2	-2	6	8	8	6	1	3	2
1	1	12	13	9	1	1	1	-2	7	5	5	6	3	2	2
1	2	40	39	9	3	2	2	-2	8	2	2	6	5	8	8
1	3	35	34					-2	9	5	4	6	6	8	8
1	4	8	8		H=	-2		-2	10	2	2	6	7	1	2
1	5	17	19					-1	1	2	0	7	1	2	2
1	6	20	19	-9	1	1	1	-1	2	36	34	7	2	10	10
1	7	1	1	-9	2	2	1	-1	3	18	18	7	3	10	10
1	8	1	1	-9	3	2	2	-1	4	13	11	7	4	2	2
2	1	28	27	-9	4	1	1	-1	5	21	20	7	5	3	3
2	2	2	3	-8	1	3	2	-1	6	8	8	7	6	4	4
2	3	35	33	-8	2	3	4	-1	7	4	4	8	1	4	4
2	4	2	2	-8	4	4	4	-1	10	2	2	8	2	4	4
2	5	13	13	-8	7	2	2	0	1	9	11	9	3	3	3
2	6	5	5	-7	2	1	1	0	2	48	49				
2	7	4	4	-7	3	2	2	0	3	5	5		H=	-1	
2	8	4	4	-7	4	2	2	0	4	2	1				
3	1	17	19	-7	5	8	8	0	5	6	7	-9	1	5	5
3	2	8	7	-7	6	1	1	0	6	4	4	-9	2	2	2
3	3	1	1	-6	2	23	23	0	7	8	7	-9	3	2	2
3	4	4	3	-6	3	11	11	0	8	8	7	-9	4	4	4
3	5	6	5	-6	4	4	4	1	1	36	35	-9	5	2	2
3	6	1	1	-6	5	5	5	1	2	0	0	-8	1	5	5
3	7	2	1	-6	7	3	3	1	3	40	47	-8	2	7	7
3	8	10	12	-5	1	13	13	1	4	28	28	-8	3	2	2
3	9	3	3	-5	2	9	10	1	5	5	5	-8	4	3	3
4	1	11	10	-5	3	10	9	1	6	3	3	-8	5	4	4
4	2	14	13	-5	4	7	7	1	8	2	2	-8	6	3	3
4	3	10	10	-5	5	15	16	1	9	2	2	-8	7	1	1
4	4	3	3	-5	6	2	3	2	1	44	44	-7	1	5	5
4	5	3	3	-5	7	2	1	2	2	21	20	-7	2	2	2
4	6	4	3	-5	8	1	1	2	3	14	14	-7	3	1	2
4	7	8	9	-5	9	4	4	2	4	7	9	-7	5	6	6
4	8	3	3	-4	2	27	26	2	6	3	4	-7	6	3	3
5	1	3	2	-4	3	5	6	2	8	3	3	-7	8	2	2
5	2	6	6	-4	4	3	3	2	9	4	4	-6	1	11	11
5	3	22	21	-4	5	14	14	2	10	2	2	-6	2	7	7
5	4	8	8	-4	6	8	7	3	1	27	26	-6	4	11	12
5	5	4	4	-4	7	3	2	3	2	4	5	-6	5	7	7
5	6	2	3	-4	8	1	1	3	3	7	8	-6	6	3	3
5	7	6	6	-4	10	5	5	3	4	2	3	-6	7	2	2

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-5	1	23	23	2	4	11	12	-5	2	11	10	2	0	45	45
-5	2	9	9	2	5	13	13	-5	3	3	2	2	1	6	7
-5	3	17	17	2	7	7	8	-5	4	4	4	2	2	8	8
-5	4	3	3	2	8	3	4	-5	5	1	2	2	3	23	26
-5	5	7	7	3	1	14	13	-5	6	9	9	2	4	8	9
-5	7	3	2	3	2	3	2	-5	7	1	1	2	6	3	4
-5	8	4	5	3	3	23	23	-5	8	9	8	2	8	2	3
-5	9	1	2	3	4	9	9	-5	9	3	2	3	0	42	42
-4	1	11	10	3	5	2	2	-4	1	2	2	3	1	10	9
-4	2	7	6	3	7	1	1	-4	2	13	14	3	2	3	4
-4	3	7	6	3	8	2	2	-4	3	14	14	3	3	15	16
-4	4	15	16	4	1	3	3	-4	4	15	15	3	4	13	17
-4	5	9	9	4	2	6	5	-4	5	9	9	3	5	4	4
-4	6	4	3	4	3	11	10	-4	6	1	1	3	6	5	6
-4	7	3	3	4	4	11	10	-4	8	5	5	4	0	25	23
-4	8	4	4	4	5	4	5	-3	1	21	20	4	1	1	1
-4	9	3	3	4	7	1	2	-3	2	7	6	4	2	9	10
-3	1	22	22	5	1	6	6	-3	3	3	3	4	3	11	13
-3	2	27	27	5	2	11	10	-3	4	1	2	4	4	4	5
-3	3	15	14	5	3	9	9	-3	5	3	2	4	5	4	4
-3	4	13	14	5	4	6	6	-3	6	1	1	4	6	2	2
-3	5	12	11	5	5	5	5	-3	7	6	7	5	0	5	5
-3	7	3	2	5	6	1	1	-3	8	3	3	5	1	5	5
-3	8	3	2	5	7	3	3	-2	1	8	7	5	2	6	5
-2	1	32	32	6	1	3	3	-2	2	24	22	5	3	15	14
-2	2	22	21	6	3	15	15	-2	3	13	12	5	4	4	4
-2	3	9	9	6	4	4	4	-2	4	27	26	5	5	4	4
-2	4	28	27	6	5	5	5	-2	5	6	6	5	6	2	1
-2	5	13	12	7	1	1	1	-2	7	3	2	6	0	7	8
-2	6	1	1	7	3	11	11	-2	9	1	2	6	1	15	16
-2	7	5	6	7	4	6	6	-1	1	61	60	6	2	7	7
-2	9	3	3	8	1	1	2	-1	2	10	10	6	3	4	4
-1	1	40	40	8	2	2	2	-1	3	19	18	6	5	5	5
-1	2	4	4					-1	4	8	7	7	1	6	6
-1	3	33	31		H=	0		-1	5	25	23	7	2	9	9
-1	4	22	21					-1	6	5	5	7	3	1	2
-1	5	9	7	-9	1	5	5	-1	7	1	0	8	0	5	5
-1	6	10	9	-9	2	5	4	-1	8	1	2	8	1	4	4
-1	7	3	3	-9	4	2	2	-1	9	3	4	8	2	3	2
-1	8	5	5	-8	1	3	4	0	1	21	19	9	0	3	3
0	3	44	45	-8	3	4	4	0	2	8	5	9	1	3	2
0	4	5	5	-8	4	3	4	0	4	29	27				
0	5	4	3	-8	5	2	2	0	5	6	6		H=	1	
0	6	2	2	-8	6	2	1	0	6	4	3				
0	7	1	1	-7	1	7	7	0	7	3	3	-9	0	2	2
0	8	2	2	-7	3	8	8	0	8	10	10	-9	1	2	2
1	1	56	56	-7	4	5	6	1	0	29	30	-9	4	3	3
1	2	32	39	-7	5	2	2	1	1	24	26	-9	5	1	1
1	3	2	2	-7	6	3	3	1	2	12	12	-8	0	2	3
1	5	15	16	-7	8	2	2	1	3	25	26	-8	1	4	4
1	6	1	0	-6	1	11	12	1	4	3	3	-8	2	2	3
1	7	7	7	-6	2	1	1	1	5	7	7	-8	3	3	3
1	9	6	7	-6	4	2	2	1	6	3	3	-8	5	2	2
2	1	7	7	-6	5	1	1	1	7	6	7	-7	0	1	1
2	2	7	7	-6	7	2	2	1	8	3	2	-7	2	4	4
2	3	7	7	-5	1	2	2	1	9	1	1	-7	3	1	1

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-7	4	3	4	0	6	4	4	-7	4	2	3	1	1	2	3
-7	7	3	2	0	9	4	3	-6	0	11	12	1	2	9	9
-6	0	6	6	1	0	41	40	-6	1	7	7	1	3	12	13
-6	2	8	8	1	1	9	10	-6	2	3	3	1	4	3	3
-6	3	6	7	1	2	4	5	-6	3	12	12	1	5	10	10
-6	4	1	2	1	3	29	28	-6	4	2	1	1	6	4	4
-6	5	9	9	1	4	12	12	-6	5	9	9	1	7	3	3
-6	6	3	3	1	5	4	4	-6	6	5	4	2	0	40	38
-6	7	3	3	1	7	6	6	-6	7	3	3	2	1	24	22
-6	8	6	6	1	8	3	2	-5	0	5	5	2	2	2	2
-5	1	16	18	2	0	50	49	-5	1	3	3	2	3	2	2
-5	3	4	4	2	1	11	12	-5	2	2	3	2	4	15	16
-5	4	14	14	2	2	5	4	-5	3	6	7	2	5	1	0
-5	5	6	6	2	4	2	1	-5	4	14	14	2	6	4	3
-5	6	8	8	2	5	3	4	-5	5	1	1	3	0	10	9
-5	7	3	2	2	6	4	5	-5	6	2	2	3	1	4	4
-5	8	2	2	2	8	3	3	-5	8	4	3	3	3	9	10
-4	0	28	27	3	0	27	27	-4	0	1	1	3	4	7	7
-4	1	32	31	3	1	4	3	-4	1	10	9	3	7	3	4
-4	2	9	9	3	2	17	16	-4	2	14	14	4	0	7	7
-4	3	4	4	3	3	10	10	-4	3	12	12	4	1	1	1
-4	4	3	3	3	4	4	4	-4	4	7	7	4	2	9	9
-4	5	1	2	3	5	3	3	-4	8	2	1	4	3	6	6
-4	6	9	9	3	7	2	2	-3	0	47	47	4	5	3	2
-4	8	3	2	4	0	30	29	-3	1	1	0	5	0	2	1
-3	0	5	5	4	1	9	9	-3	2	11	11	5	1	10	10
-3	1	47	46	4	2	1	0	-3	3	5	5	5	2	8	8
-3	2	16	15	4	3	2	3	-3	4	12	11	5	3	5	5
-3	3	19	19	4	4	6	7	-3	6	1	1	5	4	5	5
-3	4	8	7	5	0	8	8	-3	7	2	2	6	0	13	13
-3	5	7	7	5	1	2	3	-3	8	4	4	6	1	16	16
-3	6	1	2	5	3	7	8	-2	0	5	6	6	2	8	8
-3	8	1	2	5	4	5	5	-2	1	42	41	6	3	3	3
-2	0	63	61	5	5	2	2	-2	2	5	6	7	0	2	2
-2	1	47	47	5	6	1	0	-2	3	7	7	7	1	3	3
-2	2	33	32	6	0	25	25	-2	4	13	14	7	2	2	1
-2	3	1	1	6	2	2	2	-2	5	4	4				
-2	4	1	2	6	3	14	14	-2	6	2	2		H=	3	
-2	5	8	6	6	4	3	3	-2	7	3	3				
-2	6	3	4	6	5	2	1	-2	8	3	2	-9	2	1	1
-2	7	4	4	7	0	7	7	-1	0	29	27	-8	0	5	5
-2	8	6	6	7	3	4	4	-1	1	8	9	-8	1	4	5
-1	0	7	9	8	0	5	5	-1	2	1	2	-8	2	3	2
-1	1	37	36	8	1	3	4	-1	3	11	11	-8	4	4	4
-1	2	14	12	8	2	4	4	-1	4	13	13	-8	5	2	2
-1	3	36	33	9	0	3	2	-1	5	6	6	-7	2	6	7
-1	4	4	3					-1	6	2	2	-7	5	1	2
-1	5	2	2		H=	2		-1	7	3	3	-7	6	2	2
-1	6	8	8					0	0	51	52	-6	0	6	7
-1	7	5	6	-9	2	1	1	0	1	16	15	-6	1	4	4
0	0	28	28	-8	0	3	3	0	2	2	2	-6	2	2	2
0	1	13	14	-8	1	1	1	0	3	9	9	-6	3	2	3
0	2	24	23	-8	2	6	7	0	4	12	12	-6	5	12	12
0	3	7	7	-8	3	4	4	0	6	3	4	-6	6	4	4
0	4	16	15	-8	4	2	2	0	7	5	5	-5	1	7	7
0	5	1	2	-7	1	2	2	1	0	2	2	-5	2	22	22

Table 8. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-5	3	2	3	3	0	8	8	-3	4	14	14	-7	1	3	3
-5	4	8	9	3	1	1	1	-3	5	4	4	-7	2	3	3
-5	5	14	14	3	2	9	8	-2	0	8	7	-7	3	3	3
-5	6	9	9	3	3	3	2	-2	1	18	17	-7	4	6	6
-5	7	2	2	3	4	2	2	-2	2	3	3	-6	0	8	8
-4	0	14	13	4	0	8	7	-2	3	17	17	-6	1	13	14
-4	1	30	30	4	1	4	4	-2	4	2	2	-6	2	14	14
-4	2	7	7	4	2	5	5	-2	6	2	2	-6	3	3	2
-4	3	2	2	4	3	8	8	-2	7	1	1	-5	0	13	13
-4	5	6	6	4	4	8	8	-1	0	13	12	-5	2	13	13
-4	6	1	1	4	5	2	1	-1	1	13	14	-5	3	7	7
-4	7	2	2	5	0	2	2	-1	2	5	6	-5	4	5	5
-4	8	2	2	5	1	8	8	-1	3	2	1	-5	6	3	3
-3	0	41	41	5	2	8	8	-1	4	3	4	-4	0	15	15
-3	1	1	2	5	3	2	2	-1	5	6	6	-4	1	1	1
-3	2	1	1	5	5	1	0	-1	6	3	3	-4	3	10	10
-3	3	1	1	6	0	7	7	-1	7	2	2	-4	4	4	4
-3	4	3	3	6	2	2	2	0	0	14	13	-3	0	8	9
-3	5	2	2	7	2	1	1	0	1	15	16	-3	1	8	8
-3	6	2	1					0	2	2	3	-3	2	3	3
-3	7	3	2		H=	4		0	3	1	2	-3	3	11	11
-3	8	2	1					0	4	6	7	-3	4	4	4
-2	0	10	8	-9	0	4	3	0	5	11	11	-3	5	4	4
-2	1	9	9	-9	1	1	2	0	6	5	4	-3	6	1	2
-2	2	23	22	-9	2	3	3	0	7	5	4	-2	0	11	11
-2	3	4	3	-9	3	5	4	1	0	31	29	-2	1	3	3
-2	4	1	1	-8	1	5	5	1	1	3	3	-2	2	3	3
-2	5	10	10	-8	3	1	2	1	2	5	6	-2	3	11	12
-2	6	4	4	-8	5	5	5	1	3	4	3	-2	4	13	14
-1	0	22	21	-7	0	7	6	1	5	12	12	-2	5	3	4
-1	1	2	3	-7	1	1	2	2	0	16	14	-1	0	44	43
-1	2	10	7	-7	2	4	4	2	1	7	7	-1	1	2	2
-1	3	15	14	-7	3	1	1	2	2	2	2	-1	2	7	6
-1	4	5	5	-7	4	5	6	2	3	2	3	-1	3	5	5
-1	5	6	6	-7	5	3	3	2	4	10	10	-1	4	10	9
-1	8	3	2	-6	0	1	1	3	0	2	1	-1	5	4	4
0	0	57	58	-6	1	7	7	3	1	2	2	-1	6	5	5
0	1	15	15	-6	2	3	3	3	3	17	16	0	0	18	19
0	2	2	2	-6	3	23	24	3	4	4	4	0	1	3	2
0	3	5	5	-5	0	18	18	3	5	1	1	0	2	6	6
0	4	3	3	-5	1	9	8	4	0	2	2	0	3	25	25
0	5	4	4	-5	2	2	2	4	1	5	5	0	4	6	6
0	6	4	4	-5	3	14	13	4	2	14	14	0	6	6	6
1	0	13	13	-5	4	17	17	4	3	5	5	1	0	10	9
1	1	2	2	-5	5	1	2	5	1	3	3	1	2	2	2
1	3	7	8	-5	6	1	1	5	3	4	3	1	3	23	23
1	4	6	5	-4	0	2	1	7	0	1	1	1	4	11	11
1	5	5	5	-4	1	5	5					1	6	2	1
1	6	2	1	-4	2	7	7		H=	5		2	0	1	0
1	7	2	2	-4	3	10	10					2	1	1	1
2	0	28	26	-4	4	8	8	-9	0	5	6	2	2	14	15
2	1	9	8	-4	5	4	4	-9	2	2	2	2	3	7	7
2	2	19	19	-4	6	2	2	-8	0	4	4	2	4	1	1
2	3	2	1	-4	7	3	2	-8	3	6	7	2	5	3	2
2	6	3	2	-3	1	13	13	-8	4	1	1	3	0	1	2
2	7	4	3	-3	3	4	3	-7	0	7	6	3	1	7	7

Table 8. (Continued)

K	L	FO	FC
3	2	6	7
3	3	2	2
4	0	3	3
4	1	2	2
4	2	2	2
4	3	7	7
5	0	3	3
5	2	3	2
5	3	4	4
6	0	1	1
6	1	4	4
7	0	1	1
	H=	6	
-9	2	4	3
-8	0	2	2
-8	1	3	3
-8	2	3	3
-8	3	3	3
-7	0	5	5
-7	3	2	2
-7	4	3	2
-6	0	20	21
-6	2	2	2
-6	3	1	2
-5	1	2	2
-5	2	6	6
-5	3	2	2
-5	4	5	5
-5	5	2	2
-4	0	4	4
-4	1	6	6
-4	2	8	8
-4	3	6	6
-3	0	26	27
-3	1	8	8
-3	2	11	12
-3	3	10	10
-3	4	8	8
-3	5	3	3
-3	6	7	6
-2	1	7	7
-2	2	7	8
-2	3	10	10
-2	4	1	1
-2	5	1	1
-1	0	9	9
-1	2	12	12
-1	3	11	11
-1	4	1	1
-1	5	3	2
0	0	3	2
0	1	20	20
0	2	3	2
0	3	15	16
0	4	6	6
0	5	7	7
1	1	12	12
1	2	15	15
1	3	4	4
1	5	1	2
2	0	8	8
2	1	5	5
2	4	2	2
3	2	3	2
3	3	3	3
4	0	3	3
4	1	6	6
5	0	5	5
6	0	3	3
	H=	7	
-9	1	2	3
-8	0	1	2
-8	1	5	5
-8	2	2	2
-7	0	5	5
-7	1	5	5
-6	0	11	11
-5	1	9	10
-6	2	1	1
-6	3	7	7
-5	0	3	2
-5	1	2	2
-5	2	2	3
-5	4	6	6
-4	0	5	5
-4	1	4	5
-4	2	4	4
-4	3	4	4
-4	5	4	4
-3	0	3	3
-3	1	1	0
-3	2	5	5
-3	3	7	7
-3	4	3	3
-2	0	7	8
-2	1	5	5
-2	2	3	3
-2	3	4	5
-2	4	2	2
-2	5	3	3
-1	1	3	3
-1	2	3	3
-1	3	1	1
-1	4	4	4
-1	5	1	1
0	1	8	9
0	2	4	3
0	3	10	10
1	0	5	4
1	1	10	10
1	2	5	4
2	0	2	2
2	2	2	2
2	3	5	5
3	2	4	4
3	3	7	6
4	0	1	2
4	1	3	3
4	2	6	5
5	1	7	7
	H=	8	
-9	8	4	5
-8	1	2	2
-8	2	1	1
-7	0	4	3
-7	3	2	2
-6	0	9	8
-6	1	3	2
-6	2	3	3
-5	0	4	4
-5	1	4	4
-5	2	3	3
-5	3	2	2
-5	4	2	2
-4	0	7	7
-4	1	4	4
-4	2	3	3
-4	4	4	4
-3	0	2	2
-3	2	3	3
-3	3	2	2
-3	4	3	3
-2	1	2	2
-2	2	2	2
-2	4	3	3
0	0	8	8
0	1	8	8
0	2	2	2
0	3	3	3
1	0	3	3
1	1	2	1
1	2	4	4
2	0	2	2
2	1	2	2
2	2	3	3
3	0	3	3
3	1	6	6
3	2	5	5
4	0	2	1
4	1	3	2
	H=	9	
-8	0	1	1
-7	0	3	3
-6	0	2	2
-6	1	2	2
-6	2	3	3
-5	0	8	8
-5	3	1	1
-4	1	5	5
-4	2	5	5
-4	3	2	2
-3	0	6	6
-3	1	1	1
-3	3	4	4
-2	0	4	4
-2	1	1	1
-2	3	3	3
0	0	6	6
0	1	3	4
0	2	2	2
1	0	1	2
1	1	2	2
1	2	3	3
2	0	1	1
2	1	1	1
	H=	10	
-5	1	3	3
-5	2	2	1
-4	0	6	6
-4	2	3	3
-3	0	6	6
-3	2	3	2
-2	0	2	2
-1	0	2	2
-1	2	2	2
0	0	1	2
0	1	2	2
1	0	1	1
2	0	1	1
	H=	11	
-6	0	7	7
-4	0	2	2
-3	0	2	2

XXI (see Figure 14) is 2.490(6) Å or about the same as that calculated (2.51 Å) between gem-dimethyl groups in a hydrocarbon having the usual tetrahedral angle and 1.54 Å C-C bond distance. Also the distance between vicinal (essentially eclipsed) methyl groups in XXI, C(9)-C(10) or C(9')-C(10'), is 3.016(6) Å or again nearly the same value as that calculated (2.93 Å) similarly for vicinal gouche methyl groups in hexamethylethane. Thus the gem-dimethyl group effect in this spirocyclization does not seem to depend on important relief of steric compression if hydrocarbons can be taken as suitable models for organocesium compounds. Tertiary carbanions are known to have greater reactivity than primary carbanions.[37,38] Evidently the present gem-dimethyl effect is due to the destabilizing influence of methyl groups upon the tertiary carbanionic center of XXXIV and the stabilizing influence of methyl groups (especially gem-dimethyl groups) on the cyclopropyl ring[39] of XXXV.

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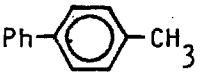
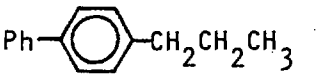
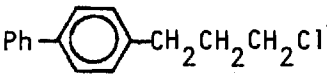
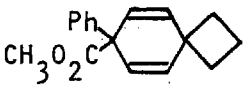
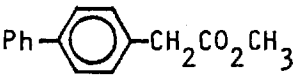
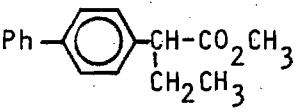
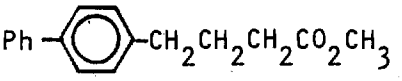
APPENDIX B

THE G. C. RETENTION TIMES OF ALL THE PRODUCTS FROM REACTIONS OF THE ALKYL CHLORIDES WITH ALKALI METALS

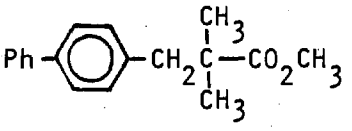
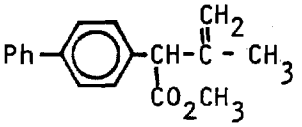
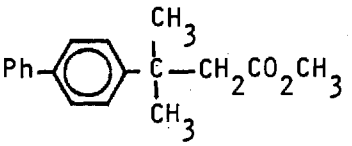
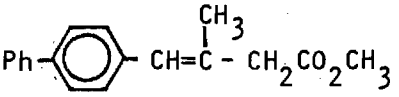
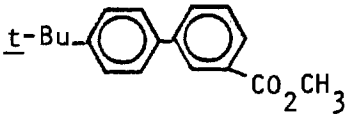
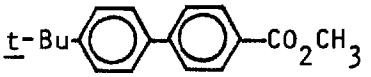
3-p-Biphenylyl-1-chloropropane

Compound	Retention Time	Relative Retention Time
	2.1	0.53
	4.0	1.00
	5.3	1.33
	7.6	0.43
	8.2	0.46
	11.8	0.66
	17.8	1.00

G. C. conditions: 3% SE-30 column, 6 ft, 1/8" diameter, column temperature 192°

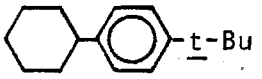
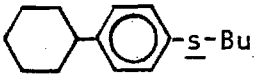
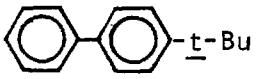
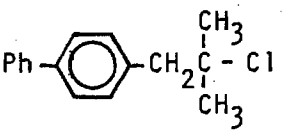
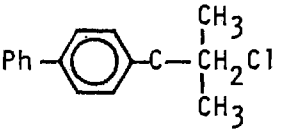
2-p-Biphenylyl-1-chloro-2-methylpropane and 1-p-Biphenylyl-2-chloro-2-methylpropane

1. Acidic Products

Compound	Retention Time	Relative Retention Time
	9.7	0.92
	9.8	0.93
	10.6	1.00
	13.9	1.31
	14.0	1.32
	14.4	1.36

G. C. conditions: 3% SE-30 column, 6 ft, 1/8" diameter, column temperature 200°.

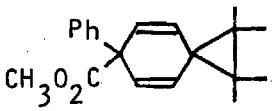
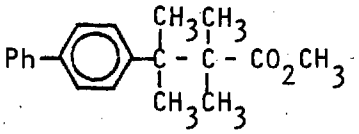
2. Neutral Products

Compound	Retention Time	Relative Retention Time
	9.0	0.70
	9.6	0.75
	12.1	0.95
	12.8	1.00
	3 peaks	1.1-2.3
	33.3	2.6

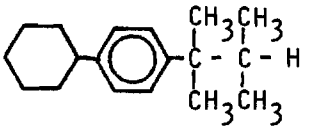
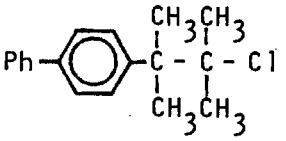
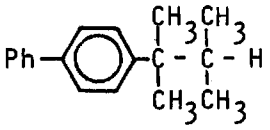
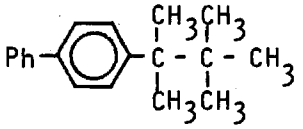
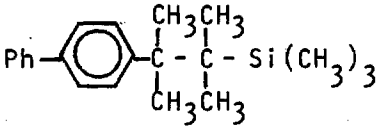
G. C. conditions: 3% SE-30 column, 6 ft, 1/8" diameter, column temperature 155°

3-p-Biphenylyl-2-chloro-2,3-dimethylbutane

1. Acidic Products

Compound	Retention Time	Relative Retention Time
	6.0	0.57
	10.6	1.00

2. Neutral Products

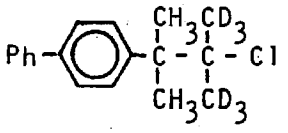
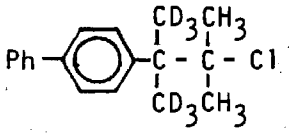
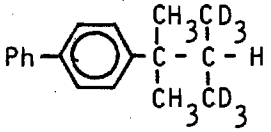
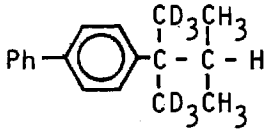
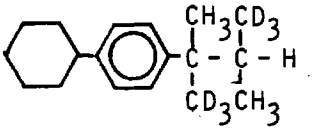
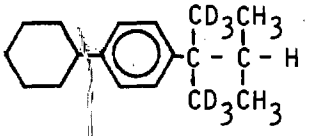
Compound	Retention Time (150°)	(190°)*	Relative Retention Time
	12.0		0.75
	14.6	6.9	0.92
	16.3	7.6	1.00
		10.4	1.37
		26.6	3.5

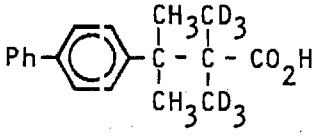
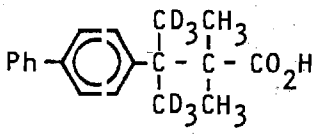
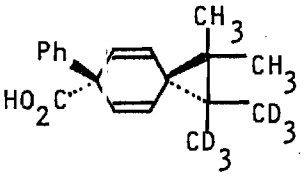
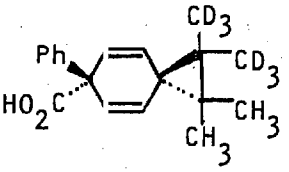
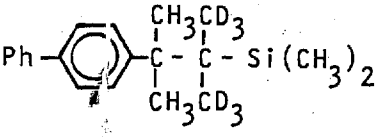
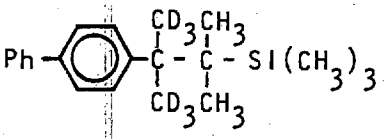
G. C. conditions: 3% SE-30 column, 6 ft, 1/8" diameter.

*Column Temperature.

APPENDIX C

NMR ASSIGNMENTS OF THE PRODUCTS FROM REACTION OF 3-*p*-BIPHENYLYL-2-CHLORO-3-METHYL-2-(METHYL-d_3)-BUTANE-1,1,1-d_3 WITH ALKALI METALS

Compound	Chemical Shift of Methyl-CH (δ)
	1.58 (s)*
	1.56 (s)
	1.24 (s)
	0.80 (d)
	1.24 (s)
	0.75 (d)

Compound	Chemical Shift of Methyl-CH (δ)
	1.53 (s)
	1.14 (s)
	1.19 (s) and 1.14 (s)
	
	1.47 (s)
	0.92 (s)

*Multiplicity.

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